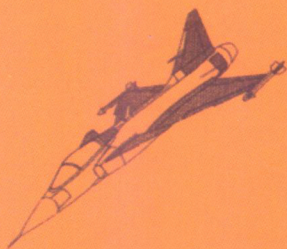
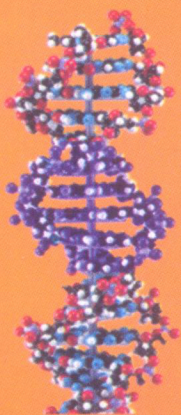
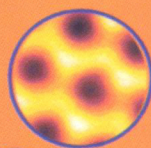


The Quest for New Materials



S.T.Lakshmikumar

The Quest *for* New Materials

S.T. Lakshmikumar



Vigyan Prasar

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The Quest For New Materials

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Foreword

The utilization of naturally available materials by all living beings had its roots in antiquity and the desire of human beings to make better materials for better tools marked the beginning of the science and technology of materials. Thus one says that human society moved from the Stone Age to the Bronze Age and later to the Iron Age. Now it seems that we are in the silicon and plastics age. When the understanding of materials was rudimentary, the tools used by the human beings were very simple stone artifacts, but the use of these tools was an epoch making breakthrough for the organization of human beings at that time into small communities. The speed of progress has been accelerating since then. For example the passage from the Stone Age to the Iron Age took several tens of thousands of years, whereas the passage to the silicon and plastics age has come about in less than half a century!

The young students are often fascinated by this evolution of materials, specially when it is told almost like a story with a broad perspective of physics, chemistry, biology, metallurgy, ceramics, engineering aspects and social systems. It is this excitement, which Dr. S. T. Lakshmikumar attempts to convey in this short but sweet book. The movement from natural artifacts to molecular design, the brave new world of nano-materials and nano-engineering, the interplay between sciences and engineering as well as the links with the living world are all described in a simple manner in this book. The rich collection of illustrations and figures add to the pleasure of reading and to the pleasing appearance. Admittedly one may argue that all these are known; however what is important is the manner of conveying the information in a lucid and cogent manner, which holds the attention of the readers. This is the special feature of the presentation.

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The author has long involvement in teaching and has exposed the material to selected student groups. The feedback from these people has been useful in refining the text, in the balance among the various topics and in the interlinking among them. The object of the book is to excite the curiosity of the young readers. Thus the book is not a textbook for the students but is nearer to the 'popular science' books. It introduces the topics to the students with an overview at a qualitative level, giving a platform from where the readers can launch into a serious study of any desired aspect. The student is also enabled to place the subject into the general framework of knowledge in science and engineering. It is thus a recommended supplementary reading for the young students. The fear of the unknown will be replaced by a preliminary acquaintance of the subject. The bewilderment at the diversity of the topics will be replaced by an understanding the links among the various disciplines. The students will be nicely challenged by the exposition of the diverse uses and developments of materials first, with the science background being given in small doses later in the book. In dealing with materials, almost all branches of knowledge are all knit together into one woven fabric.

The task of motivating young minds to understand the spirit of science and technology will be aided if the book is available at a reasonable cost and in an attractively produced manner. One wishes success for this effort to enrich the minds of the young students.



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&
Formerly Director, National Physical Laboratory,
New Delhi 110 012.

Acknowledgement

नमो गुरुभ्यः

*I am deeply indebted to
everyone who helped me
learn
through teaching, discussion and argument.*

Richard Feynman and Richard Dawkins have been the inspiration for attempting this work. Feynman through his memoirs and the small book "QED the Strange theory of light and matter" had shown how to bring the depth and beauty of scientific understanding to the general public. Among all the books of Dawkins, "The River out of Eden" showed me how an explanation of contemporary science can be made exciting and highly readable. Whatever little merit may be found in this little attempt of mine can be traced to the influence of these two scientists. Being inspired by the divine is no guarantee for success. I would be obliged if the readers bring to my notice shortcomings and errors in this book..

I am indebted to Prof. N. Mukunda of the Indian Institute of Science Bangalore for a meticulous reading of the last chapter and a series of corrections and to Prof. Simon P Ringer for pointing out an error in the discussion on strengthening of materials. Dr S M Shivaprasad has always spared a lot of time for discussions and made many helpful suggestions for which I am grateful. I am also obliged to Dr R. Bhattacharyya, Dr T D Senguttuvan, Shri S U M

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Rao, Shri Vipin Kumar and other colleagues at NPL who have taken the trouble of reading the manuscript and making suggestions and corrections.

I am obliged to the researchers and publishers who have kindly given permission to use their photographs and pictures for illustration. Mr. Sameer Khanuja had very kindly helped me in improving the pictures and designed the attractive front cover for which I am very much in his debt. I am grateful to the National Physical Laboratory and to the successive directors of NPL for enabling my growth as a scientist all these years. I also thank Vigyan Prasar for supporting the publication of this book.

Lastly and most importantly, I would like to thank Prof. E S Raja Gopal for writing a foreword to the book and for his continuous encouragement and help during the writing of this book.

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March, 2005

New Delhi

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Publisher's Note

Vigyan Prasar has been bringing out publications on a variety of topics of Science and Technology. Popular Science Classics, India's Scientific Heritage, Natural History, Health and Do-It-Yourself are some of the series that have evolved over the years. Our emphasis has been on bringing out quality publications on various aspects of Science and Technology at affordable prices. Further, Vigyan Prasar is putting in efforts to bring out publications in all major Indian languages for various target groups.

The present book, **The Quest for New Materials** by Dr. S.T. Lakshmikumar, scientist working in the National Physical Laboratory, New Delhi, is a story of human endeavour to develop new materials. The author starts with an overview of the never-ending quest for new materials since the Stone Age. The book brings out clearly the role of science and engineering in the development of new materials. The main objective of the book is to narrate to the readers the exciting story of development and uses of materials brought about through an interplay between different disciplines of science and engineering. The world of materials is really a fascinating one. Its diversity is truly amazing. Although the topics of six chapters may apparently appear to be unconnected but as one goes through the different chapters the underlying links among the various topics would become obvious. A major attraction of the book is a large collection of beautiful illustrations. The book would be useful to students, teachers, lay-persons having interest in science and even to the researchers in the field. Any suggestion for the improvement of the book would be welcome.

Vinay B. Kamble
Director

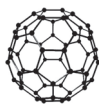
Introduction

This is an attempt to share the excitement in the development of materials science with children who have an exposure to science at the secondary school level. The latest developments in the fields of materials science are presented here as a story of human endeavor to develop new materials. Since a brief and coherent presentation is necessary, arbitrary selection of material based on personal assessment had become inevitable.

The material has been organized into six chapters. Each is complete and offers a coherent narrative. The first of these is an overview of the quest for new materials where the human efforts starting with the use of naturally occurring materials for starting the human cultural evolution and ending with the current approach of molecular design are reviewed. The presentation seeks to show a series of steps along which the human efforts have reached the current heights. The next chapter on nanomaterials and nanomachines provides a more detailed understanding of the recent excitement in this area, which has become a major attraction for the scientific community. Since these two chapters seek to provide a coherent exciting story, it became necessary to assume that the reader is familiar with science. Basics of chemistry, materials characterization and biological science are required for an understanding of these two chapters. It is not possible to provide all these without spoiling the flow of the narrative. In any case, the examination orientation of the school curriculum does not emphasize the basic beauty and coherence of science nor the latest developments in these areas which have provided the basis for the development of new materials. For these

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reasons, the next three chapters cover the basic concepts of chemistry, techniques of probing matter and the physics of living. These largely answer the queries and doubts that may occur in the first two chapters. Hopefully these would also serve as exciting introductions to the basic concepts of science, in addition to demonstrating the role of basic science in the development of materials. The final chapter seeks to describe the experimental underpinning of physics. The whole enterprise of science is experimental in origin and not surprisingly the framework of modern physics is also defined by the demands of experimental science. Understanding this is very essential to appreciate the beauty and coherence of the scientific enterprise. The material presented here therefore begins with the feeble attempts of the humans to make better tools and ends with a description of comprehensive theories of physics.



II From Nature to Molecular Design

Making and using Tools

Man is a tool-using animal. Using a tool demands foresight. The user must have a goal in mind and be able to recognize that using the tool will help in realizing the goal. When a stone is used to break open a nut, the stone is a tool. The desire for the contents of the nut motivates the use of the stone. Tool usage demands planning. Equally importantly, it is necessary to have a proper understanding of the properties of the material of which the tool is made. In the above example, a ball of mud cannot be used to break the nut. A hard stone is needed. When the properties of the material are evaluated, materials science begins. Thus science of materials is the oldest science. It begins as soon as a tool is used. However simple the tool may appear to the modern human society, a science of materials exists behind tool usage.

Man is not the only tool-using animal. Jane Goodall observed that chimpanzees poke blades of grass and small twigs into termite holes. When the termites crawl onto the twig, the chimpanzee eats the termites. Figure II.1 on colour plate i (Page 10/11) shows a chimpanzee eating termites he has fished out of the termite hole. When this observation was brought to the notice of the famous hunter of human fossils, Leakey, he reportedly observed that we should either change the definition of man as a tool-using animal or invite the chimpanzees to the United Nations! It is obvious that the chimpanzee was altering the normal state of a material, namely removing the leaves of the twig. It is using the twig for a new purpose of its own, namely to fish termites; obviously an example of tool usage.

It appears that science of materials is not merely the oldest science; it perhaps is the only science that is known to other species. Obviously the chimpanzee knows a few things about the twigs. It knows that it has to use a twig of a suitable size. The twig has to be put in the termite hole and later into its own mouth. A large stick will obviously be not very useful. A twig from a plant which has thorns cannot be used as the chimpanzee could hurt itself. There cannot be any gum or milk oozing from the twig since the termites would get stuck in it. Also the mud from the termite hill could stick to the twig. Perhaps it would be preferable to use a twig which does not have a bad taste. For example a twig from a neem tree would be undesirable. Of course, this assumes that the sense of taste of the chimpanzees is similar to us humans. It probably is. They also prefer sweet fruits. The above discussion serves the basic purpose of bringing into focus the fact that even to use a simplest tool, an understanding of the material being used is very important.

Chimpanzees in the wild have shown so much variety in behavior that it is now accepted that chimpanzees have some sort of a “proto” culture. Leakey may not have been far off calling for them to be admitted to the United Nations. Several interesting tool usages observed in chimpanzees are listed in Table I. These include the use of levers and fly catchers. The table shows that some of these behaviors are observed with certain groups of chimpanzees and not among others. This is a good reason to identify these as cultural tool usage practices and not instinctive behavior.

These observations raise some questions that cannot be easily answered. Can the behavior of other animals be also classified as tool usage? Modern study of animal behavior has given several wonderful examples. It has been observed that birds drop shells and mollusks on hard stones to break the outer shell and thereby gain access to the edible inner meat. More surprisingly, during the period when milk was delivered in glass bottles, some birds learnt to open the cover and drink the cream floating on top. Curiously, this behavior was copied by other species of birds. Monkeys developed by themselves the ability to throw seeds mixed with sand into the water and then eat the floating seeds and to wash tubers and roots to remove

Table II.1 Tool usage in Chimpanzees

Observed Behavior	Location of the Chimpanzees					
	Bossou Guinea	Tai IvoryCoast	Kibale Uganda	Budongo Uganda	Gombe Tanzania	Mahale Tanzania
Dig termite nest using stick as a spade	✓					
Using wood/stone hammer and anvil		✓				
Fishing for termites using leaf materials					✓	✓
Use sticky leaves as whisks to catch flies		✓		✓	✓	
Use sticks as levers to enlarge entrance		✓			✓	
Use a branch to hook another	✓					
Using leaves for cleaning body and wounds		✓	✓		✓	✓

the mud. They could even train succeeding generations to do this. Most primates could even be trained to use the sign language developed for the human deaf and dumb. These are examples of exciting modern investigations on animal behavior. The meaning of these studies and the use of such evidence for demanding “animal rights” is strongly debated.

Human use of Natural materials

While the use of tools by other animal species, in particular the chimpanzees is interesting, even the earliest human or hominid tools are distinctly superior. The oldest stone tools found are dated to about 2.4 million years ago. Stones were chipped to form sharp chopping or cutting edges. These are typically made from crystalline rocks such as basalt, quartz or chert. These stones are formed at very high temperatures and pressures inside the earth. They are much stronger than sedimentary rocks formed on the earth surface. If the stone is

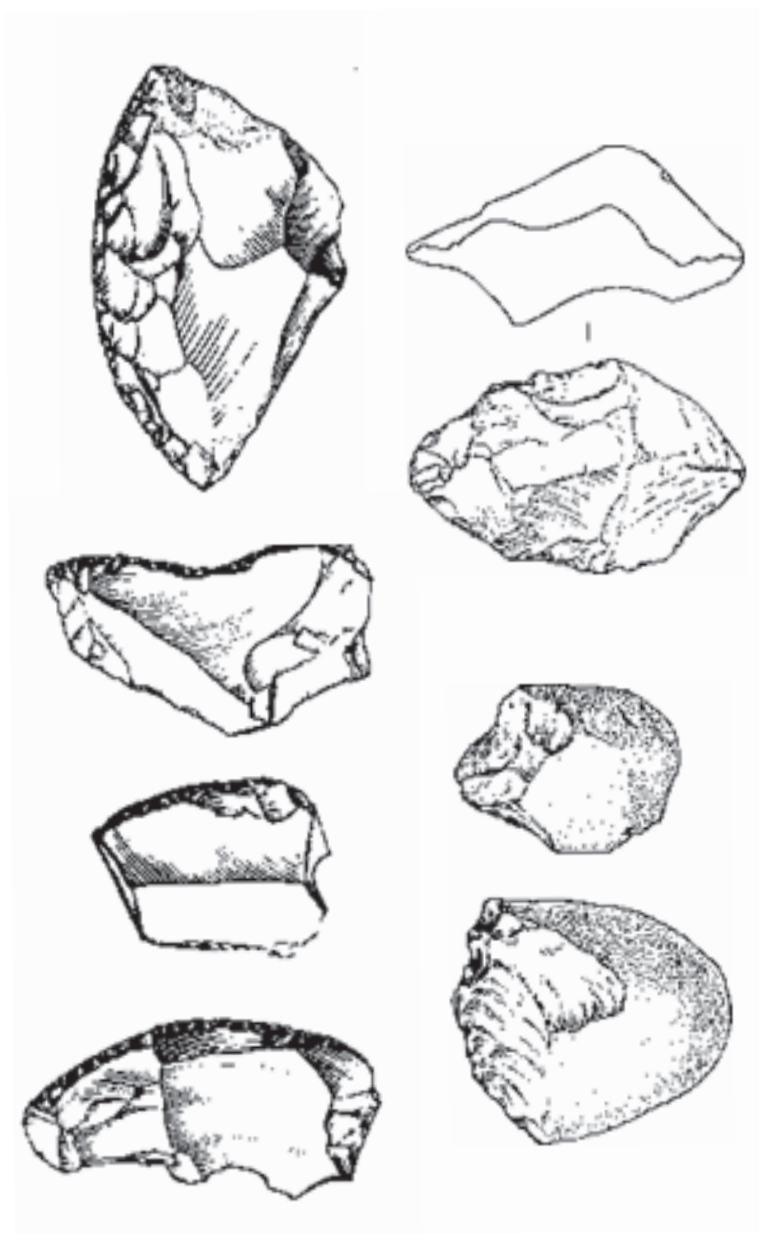
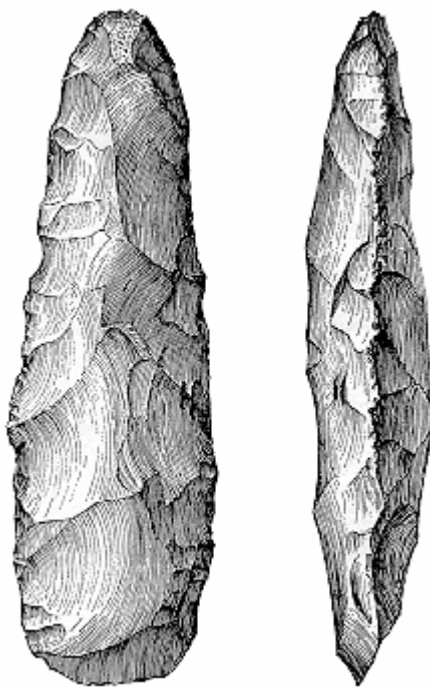


Fig. II. 2 . Representative examples of old stone tools.

not extremely hard, the sharpness of the stone tool will be lost very quickly. This selection of stones clearly indicates that the early humans had an understanding of the superior strength of these stones. Evidence suggests that these stone tools were used for cutting, scrapping and opening the bone marrow cavities. Some examples of simple stone tools are shown in Figure II.2. The use of bone and horns for digging has also been confirmed. In Africa, Europe and the near east, more sophisticated stone tools have emerged between 1 million and 200,000 years ago. These are represented by the easily recognized stone hand axe with its two surfaces being shaped to provide a double sided cutting edge. The shape and size is suitable for holding by hand. Such axes were also hafted or tied to wooden handles. The front and side views of a representative example of a hand axe are shown in Figure II.3. Clearly such a tool is more complex and clearly different from the older stone tools shown in Figure II.2.



*Fig. II. 3 The stone axe with a double sided edge.
The front and side views are shown*

However, there have been significant periods over which the techniques of making the tools and the design of the tools have remained static. The Stone Age men in china and java continued to use the old stone tools right till the advent of modern man less than 100,000 years ago. It is now confirmed that the modern man, the ancestor of all humans now living on earth, emerged in Africa around 130,000 years ago and has displaced the earlier human species by about 30,000 years ago. After this, the techniques of making the tools have been improved and made very complex. For example, the technique of heating and suddenly cooling flint stones had been developed to shatter the stone in a controlled way and obtain a very sharp edge. Methods evolved for sharpening the tools for reuse. Beads, fish hooks, arrow heads, spear points and sewing needles all appear very early in the history of modern man. Some complex tools are shown in Figure II.4.

The superior tools used by man since the last 100,000 years probably permitted a larger population to be supported and helped in displacing the earlier human species. Agriculture and a stationary life style largely displaced the nomadic life style for the same reason; the ability to provide food to a larger number of people. The stone

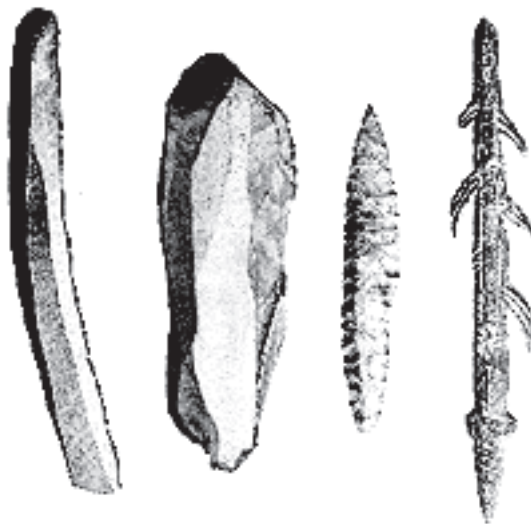


Fig. II. 4 Examples of tools of made since about 50,000 years.

tools, bone implements and presumably wooden tools, continued to be improved right till the Bronze Age 5-7000 years ago. One significant point remains unaltered. The materials were all naturally occurring. The materials science of that period was limited to the selection of suitable materials and the tools fabricated were limited by the properties of materials available in nature.

The knowledge of the properties of naturally occurring materials and techniques of using them to make high quality tools resulted nonetheless in a very sophisticated culture. The best illustration of the sophistication is obtained by the analysis of a human body found in the Italian Alps in 1990. The hunter was probably injured and trapped in the ice. Radio carbon dating showed that the body was trapped in ice for about 5,000 years until the melting of the ice exposed the body. Since the body was trapped in the ice of the Alps, it was well preserved at the time of its discovery. Most of the implements and clothing were reconstructed from small bits and pieces that remained near the body. Careful analysis of the body showed that the man carried an axe with a Yew-wood handle and a blade made of naturally occurring copper. He used a flint blade for a knife which had an ash-wood handle, a scabbard made of bast which could be mounted on his belt. A piece of an antler was fixed to a lime tree branch and used for sharpening the flint tools. He used a hazel rod bent into the shape of a 'U' and fixed with wooden slats to serve as a back pack. He had a quantity of grass rope formed into a net for catching birds or small prey. A birch container was used to carry embers required to start a fire when required. A quiver made of chamois leather contained his arrows. The flint arrow heads were attached to the shafts with birch tar and tied with a string. He was in the process of making a two meter long bow from yew-wood branch. He possibly was having a medicine pouch with some naturally occurring birch polyporus. The clothes consisted of a cap, hide coat, grass cloak, leggings, belt, loincloth and a pair of shoes. No woven materials were used; only tanned leather and a grass coat. The stitching was with animal sinews (thin wire like parts of a muscle). The careful and systematic analysis made by the modern scientists to obtain this mass of information from a single dead body is really amazing. The

picture shown in Figure II.5 on colour plate ii (Page 10/11) was made by an artist using the information gained from scientific analysis. An actual photograph would show a highly disfigured human dead body. The scientific study enables us to appreciate the complexity of the knowledge and skill of the ancient Stone Age people. Organized training must have been needed to accumulate the skills required for making the tools and clothing. Possibly, trade for exchange of materials and tools also existed.

Similar elaborate selection of materials from different plant and animal sources is very common in surviving tribes and Stone Age societies. Specific types of wood are used for specific applications. Similarly, bones or skins from specific animals are selected for use. It should be realized that these selections cannot be universally attributed to selection based on superior performance. While it is possible for routine experience to confirm the superior strength of some wood such as from Oak, it is not possible in all the cases. The material properties will not be constant enough to permit such comparisons. Not all branches from all birch trees will be inferior or superior to all branches from all lime trees for example. It is possible that some of the very precise selection is traditional and because of local availability. These observations are in general true of all traditional technical expertise right up to the time of the industrial revolution.

Creating new materials

The materials used by man up to the start of the Bronze Age some 6,000 years ago were all natural. The progress achieved by human societies in spite of this limited availability of materials is really astounding. Man had become a farmer. By careful selection of the plants, significant improvement in the quality of the food crops was achieved. In addition, man has succeeded in domesticating animals. Pastoral way of life has even resulted in the alteration of human biology. The ability of adult humans to consume milk is observed in societies which have domesticated animals that provide milk. In societies which do not use animal milk, such as the Native Americans and some Africans, adults and even small children other than babies are lactose intolerant. They cannot digest milk. This prevents the elder



Fig. II. 1 Photograph taken by the scientists at the Jane Goodall Institute of a chimpanzee eating the termites from a twig.



Fig. II. 5 . An artist's image based on the scientific examination of the body of the stone age ice man found in the Italian alps. The complex technological capabilities are visible. (Used with permission of the South Tyrol Museum of Archaeology).

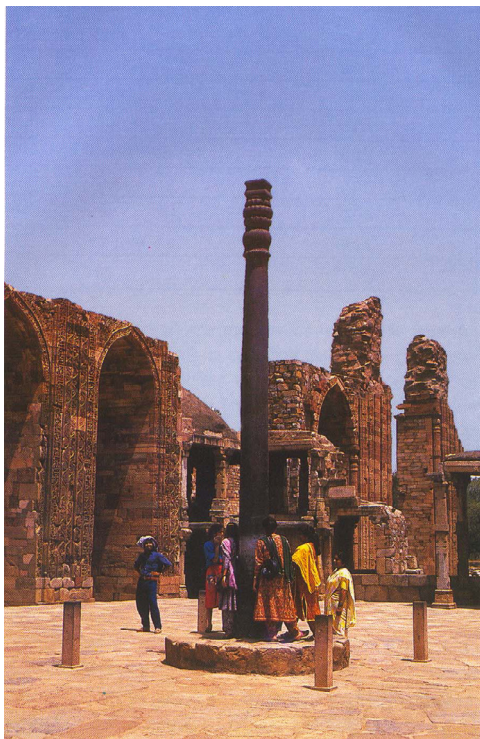


Fig. II. 6 The Delhi Iron pillar is an exquisite example of the glories of ancient trial and error technologies. (Used with permission of Prof. T R Anantharaman).

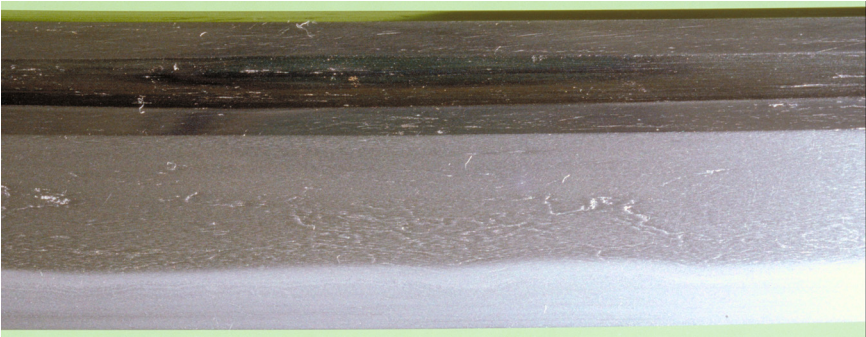


Fig. II. 7 The microscopic pattern of the grains of iron in a typical Japanese sword. The wood grain pattern reveals the many layers formed by repeated forging. (Used with permission of Dr. Lee A Jones).

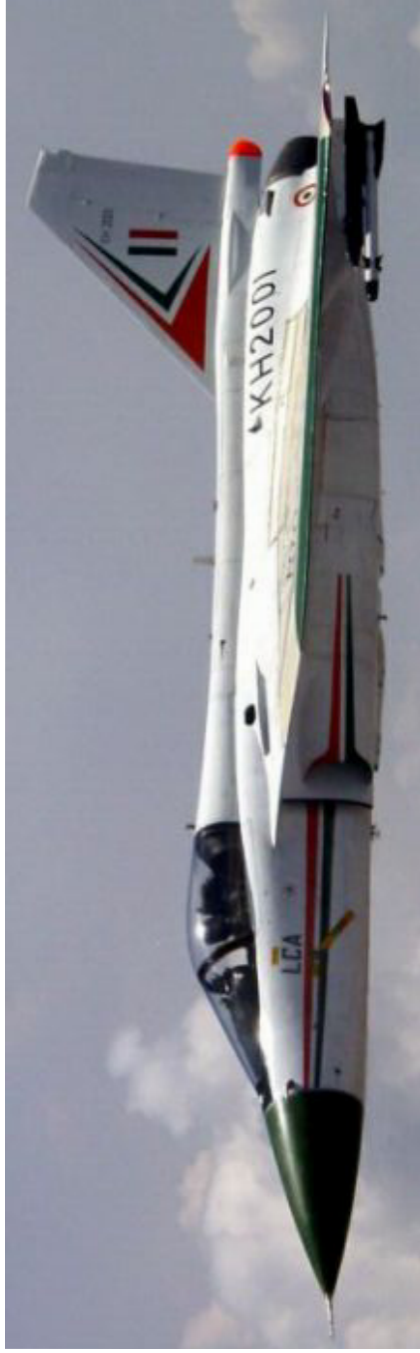


Fig. II. 12 . The Indian Light Combat Aircraft (LCA) is a typical modern military aircraft which has wings, fins and other parts made of light weight carbon fiber reinforced composites

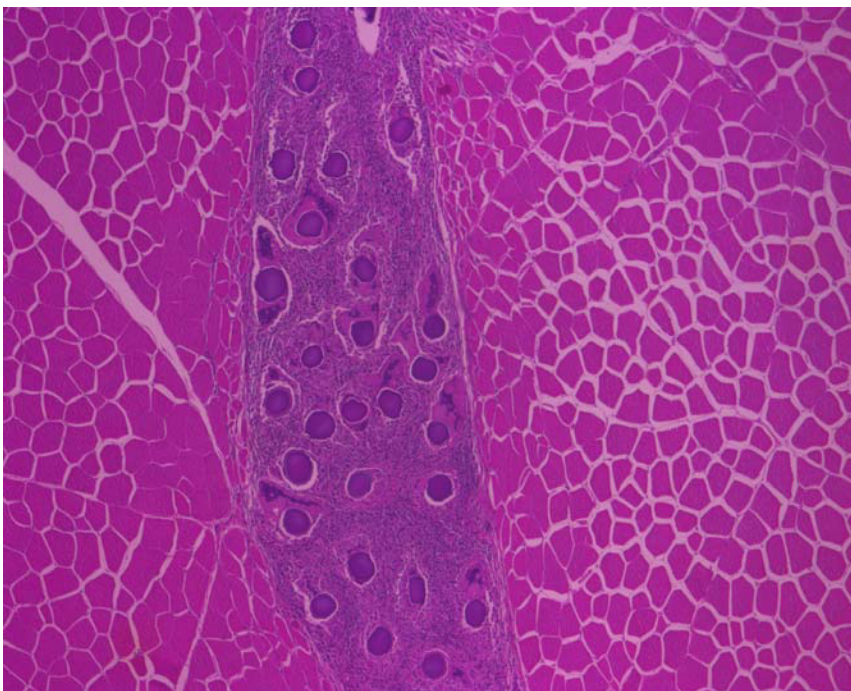


Fig. II. 20 A monofilament of Bio-steel® embedded in muscle tissue as part of the experimental verification of biocompatibility by Dr Jeffrey Turner of Nexio Biotech

children from competing with the younger children for mother's milk and is called a Darwinian adaptation. In pastoral societies, the availability of milk increased the survival of the individuals who could consume milk. The example shows how even simple technical capabilities have shifted man away from his natural state. While using tools made from simple naturally occurring materials, sophisticated culture had developed. Religion flourished. Huge monuments were erected for the priests, kings or gods.

The next step in man's quest for better materials was taken in the Near East where bronze and iron were successfully made. These materials do not occur in nature. Native cultures of America, New Guinea and Australia did not develop this technology. A theory of human development due to Jared Diamond attributes this to the non-availability of domesticated draught animals in these cultures. The emergence of societies capable of developing completely new materials is thus not inevitable. In any case, bronze and then iron were the new metallic materials developed by some human societies for making superior tools.

As the example of the iceman shows, copper in metallic form is naturally occurring. It is very rare, not very strong and easily corroded. Gold occurs naturally, is extremely rare, and is too soft for use as a tool. The first important development was the conversion of copper ore into the metal and alloying it with tin to obtain bronze. Most metals occur in nature as either oxides or sulfide ores. Heating the ores in a fire which contains carbon as the reducing agent could have converted the ore into the metal. The lower melting temperature of copper permitted the melting of the metal after the ores were reduced to the pure metal. The addition of tin or other additives (antimony, arsenic etc; were all tried) resulted in the formation of strong alloys. Metallic tools superior to the stone tools permitted the advent of the ancient cultures of Egypt, Mesopotamia, China and the Indus Valley, among others.

The temperature attained with wood fires and pottery kilns was $\sim 1150^{\circ}\text{C}$. This is sufficient for melting copper alloys but not sufficient for melting Iron. Copper ore is very rare. Iron ore is more abundant. Blowing air with bellows was developed to increase the temperature

of the flame and produce iron for tools. Even with this additional step, it is not possible to melt pure iron. So, high carbon content cast iron with a lower melting point was developed. Forged iron was another development. In forging, the metal was softened at high temperature and forged or beaten on the blacksmith's anvil to make an implement or tool. Ores always have sand as an impurity. These impurities float on the top of molten metal in the form of slag. Since iron is not completely melted, the slag cannot float to the surface of the liquid metal. The hammering at high temperatures could however remove most of the impurities from the hot and soft metal. The development of cheaper and superior iron tools led to the replacement of the more ancient bronze tools and weapons. The bronze weapons however do not get rusted easily and survive, resulting in their presence in most museums.

Both bronze and iron were first produced by trial and error technologies. The importance of any of the parameters, the quality of the ore, wood or coal used as a fuel and for reducing the ore etc., were not understood. Experience was of limited help since procedures optimized for one set of materials very often did not work for a second set. With a lack of fundamental understanding of the chemical processes, this is only to be expected. The miracle is the extremely high quality of some of the products actually realized. Two examples of highly developed ancient skills in iron metallurgy are the Samurai sword and the Delhi Iron Pillar. This selection does not consider the aesthetic or cultural value of these ancient artifacts. The Samurai swords are known for providing a combination of extreme strength and flexibility. The Delhi Iron Pillar is remarkable for the low rates of rusting observed in spite of exposure to the atmosphere for over a thousand years. In both cases modern scientific analysis can explain the remarkable properties.

The Delhi Iron Pillar shown in Figure II.6 on colour plate iii (Page 10/11) is a huge artifact of the 3rd or 4th century AD. It is now located in the Qutab Minar complex in Delhi, constructed by the Delhi sultan's in the 11th and 12th centuries. The exact place where it was fabricated is not known. It has remained exposed to rain and sun for at least the last 900 years and has not rusted. During the traditional forging

process, slag or the silicate impurity is always retained in the steel to some degree. In the Delhi Iron Pillar, enrichment of phosphorus from the slag inclusion takes place at the interface with the initial rust layer. Consequently, the rust forms a thin strong film of iron Oxyhydroxide (δ -FeOOH) and phosphates which prevents corrosion. It is obvious that this understanding did not exist when the pillar was fabricated. The inclusion of the slag was accidental. It would not have been possible for the ancient workmen to identify which constituent (the ore, the fuel or the additives) is responsible for the superior performance. It would have been difficult to duplicate the results since the properties of the materials used could not be controlled. It is almost impossible to use the experience to make decisions on the suitability of alternate sources of ore or fuel at a different location. Even duplicating the actual process is not viable. It is not possible to control the materials as required, without an elaborate testing process based on modern science. If the process is economically viable, using phosphorus as an additive in a modern iron works is a better option. This is the general problem with all ancient technologies. They can fill us with admiration and pride but will not offer economically viable technologies. It would be pertinent to note that for current use, it would be preferable to use cheaper steel that can be protected by a layer of paint rather than costly steel which does not rust. Even the costliest rust proof stainless steels would be cheaper than the forging techniques used in earlier era.

The Samurai swords are extremely strong. They can slice through ordinary iron knives. At the same time, they are not brittle and do not break easily. This combination is quite difficult to obtain. Diamond is the hardest material but it is easily broken, very much like glass. The ancient Japanese craftsmen solved the problem of fabricating an extremely strong sword blade which can withstand stress during use by employing what in current technology is termed as a laminate. The usual forging process of beating the steel while it is red hot is employed. The blade after forging is folded into half and forged to the original size again. After 10 repetitions the blade would consist of 1000 ($2^{10} = 1024$) layers. If the final thickness of the blade is about 1 mm, the thickness of each layer would be as low as a micron. Figure

II.7 on colour plate iv (Page 10/11) shows the cross section of two Japanese swords. The small grains or crystallites of iron show a pattern very similar to grains in wood. Actual samurai sword blades have been formed with the final layer thickness being in the range of nanometers making them the first layered nano composites. Economically, the process is at present not viable for any practical use other than for making high cost curios for the rich. Other societies had also used the fold and forge process but had not extended the process for such a large number of steps and did not achieve the nanometer sized layers.

Systematic Development of Materials

Inability of applying the knowledge gained during one process to another, persisted with human efforts for developing new materials till the advent of modern chemistry, three hundred years ago when the trial and error methods were replaced by modern processes based on the principles of physics and chemistry. These developments were part of the renaissance in Europe when tradition was questioned and experimental observation became the basis for evaluating knowledge. Science expanded rapidly since Galileo and Newton. The basic theories of chemistry in particular, had an enormous impact on the ability to develop new materials. The work of Dalton and the chemists following him made it possible to understand the properties of the materials by considering them as elements or compounds. The processes that lead to the formation of a pure metal from one oxide ore could then be modified as required to produce a second metal. Faraday's laws of electrolysis enabled one to understand another process, electrolysis for preparing and purifying materials. The ability to quantitatively determine the properties of materials helped in the process of developing better materials and often at a very much reduced cost.

Two examples can be cited to best illustrate the improvement chemistry has made for the synthesis of new materials. In Emperor Akbar's court, ice was available. Using relay teams of horses, ice was brought to the royal court in Agra in North India from the distant Himalayas. The cost was mentioned by contemporary historians as

equal to the weight of gold. A comparison with contemporary price of ice would of course be ridiculous. At the start of the nineteenth century, the king of England decided to send a birthday gift to the prince of France. The gift was a set of aluminum cutlery. At that time, aluminum was costlier than gold. This was just before the development of the electrolytic process for the refining of aluminum. It is difficult to imagine a cheaper metal than aluminum today.

The advances in physics and chemistry over the last 100 years have improved our understanding of materials even further. It has become possible not merely conceptualize atoms and molecules but also to experimentally observe them. Using quantum mechanics it is possible to understand in more detail the electronic processes responsible for bond formation. The ability to probe matter at the atomic scale enabled further systematic study and improvement of the properties of materials. Since strength of a material is one of the important attributes for both stone tools and swords, it is useful to understand how modern knowledge helps in understanding their strength.

Unlike in a gas, in a solid, the individual atoms and molecules are very near to each other. Even the very basic properties of solids such as their fixed volume and shape are because the atoms and molecules are closely packed. Dalton's theory suggests that atoms join to form molecules and thus the compounds have properties different from those of the elements. In compound formation, each atom combines with a small number of other atoms. These will then be neighbours to one another. When the distances between atoms are reduced while maintaining the neighbours fixed by the chemical reactions, there is periodic order in three dimensions. The simplest example of such arrangements can be seen by considering the packing of two types of circles shown in Figure II. 8. When each atom of one type is surrounded by four atoms of the other type, a square order is observed. When each has six neighbors, a hexagonal packing is observed. The second type of atoms are shown as broken circles. The actual order observed in real crystals is more complex and 230 different varieties are possible. These regular arrangements of atoms are called the crystal lattices.

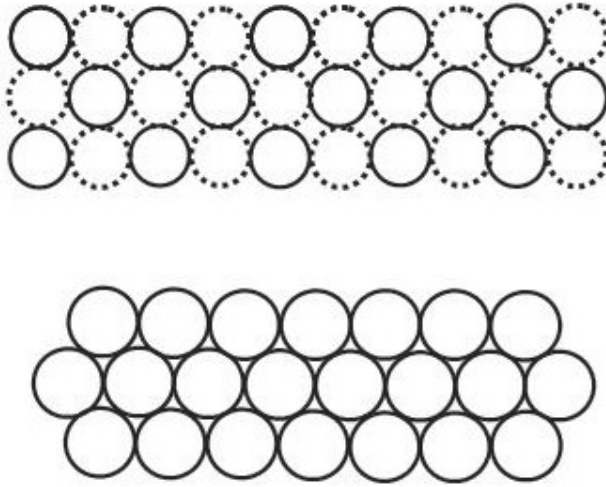


Fig. II. 8 Examples of lattices in two dimension formed with four and six nearest neighbors

Real crystal lattices will have a small number of defects. The ordering of atoms in a crystal reduces the energy of the solid. The energy of an ordered solid would be lower than that of a disordered one. As with water flowing down from a height, all processes in nature occur easily when the energy is lowered. Consequently, when a defect is created in the crystalline lattice, energy is spent. One should expect that ideally no defects would form. However, disorder is also created when a defect is formed. A more disordered state is preferred in nature. Thus the increase in energy required to form a defect is balanced against the increase in disorder. A finite number of defects remain in any real material. The fact that atoms arrange in regular lattices and that defects exist is relevant for understanding the strength of solids. One type of defect which is relevant for the present discussion of strength is called a dislocation. It is a missing row of atoms in the crystalline lattice. A model of a dislocation is shown in Figure II.9. There are six vertical layers of atoms in the upper part and only five in the lower part of the crystal. The third vertical layer from the left is a half layer. When a mechanical load is applied, the bottom part can move with respect to the upper part in the horizontal direction.

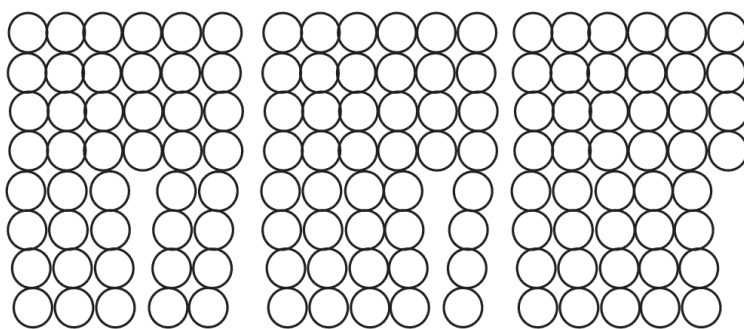


Fig. II. 9 A schematic picture of a dislocation which is a row of missing atoms in two dimensions which can easily move due to a small force

This movement will stop when the half layer comes to the end of the crystal. The half layer will then become the sixth layer from the left in the figure. This can be seen as a movement of the dislocation towards the surface. This movement of the lower part at small loads means that the solid is not capable of withstanding large loads. When dislocations move easily, the materials are soft and ductile. Metals can be easily bent because there are a large number of dislocations which can move easily. When the dislocations are prevented from moving, we get hard materials. Normal materials consist of a large number of small crystallites (also called grains) rather than a single crystal. The direction along which a dislocation moves is also different for different crystallites. Thus a material with smaller average grain size will be stronger. When a hard steel is examined microscopically it is found that a large number of small particles are distributed in the material. These particles ensure that the grains do not become large during high temperature processing. A typical microscopic particle, in this case, of Titanium Carbide (TiC) is shown in Figure II.10. The series of alternate light and dark bands seen in the micrograph are of grain boundaries pinned or prevented from growing by the microscopic particle. Small particles of iron carbide can also be used to prevent the motion of dislocations and increase strength. Trial and error methods employed earlier for improving the strength of steel can be replaced by this systematic knowledge. Advanced

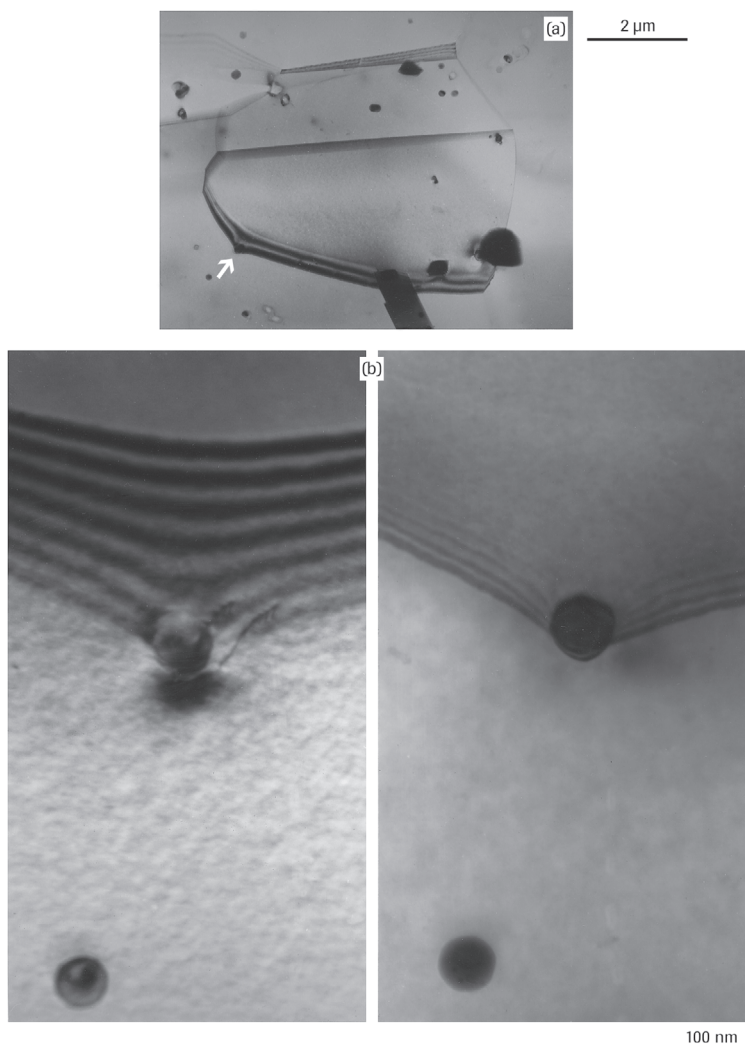


Fig. II. 10 Transmission electron micrograph of a stainless steel foil, illustrating the pinning by a TiC precipitate particle in a shrinking grain. The boundary/particle interaction is magnified in two different orientations in (b). (Used with permission of Prof. Simon Ringer).

characterization techniques can be used to identify the particles, determine their composition and systematically identify the methods of processing, which give the hardest materials.

Applying the knowledge for new systems

The extensive knowledge gained during the recent past has enabled a new approach to materials development. This involves designing a material as per the demand. This approach is the next step beyond systematically studying the materials and improving them, using concepts of physics and chemistry. Development of the fiber reinforced plastic materials illustrates the approach. As discussed above, material deformation is caused by the presence and movement of dislocations. Pinning or preventing the movement of dislocations is necessary for improving the mechanical strength of materials. A composite material can be designed with a prior knowledge of the strength to be expected and the density of the material. Fiber reinforced plastics have become a major means of reducing the weight of everything from roofs of huts to airplanes and satellites in space. The success of this approach in creating light weight and high strength materials is seen in the extensive application of carbon fiber reinforced composites for aerospace applications. As can be seen in the micrograph in Figure II.11, the material consists of a large number of

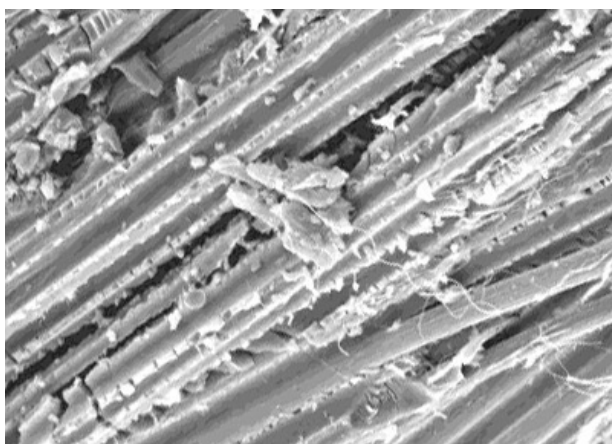


Fig. II. 11 The electron micrograph shows the fibers in a composite material

fibers which are fixed together in a matrix to transfer the stress from one fiber to another. The fiber being a material with a very high strength along the length, strong materials can be realized. The fibers can be oriented in different directions to provide strength in all directions. These composites have a higher strength and lower weight and have replaced the wings and other metal parts of a modern fighter plane. Most of the improvement in the performance of advanced military aircraft in the recent past is attributed to the extensive use of these materials. A photograph of a typical modern military aircraft, the light combat aircraft being developed in India is shown in Figure II.12 on colour plate v (Page 10/11). As with most aircrafts of this type the wings, flaps and other parts are made of carbon fiber reinforced composite rather than sheet metal. Currently, the use of carbon fibers which have diameters of a few nanometers, “carbon nanotubes” in super high strength and high thermal conductivity composites is being explored.

Principles of chemical bonding and compound formation also provide detailed systematic understanding of the strength of materials and enable the design of new materials. Figure II.13 shows the various electron energy states in carbon. A pure carbon atom has two electrons in the $1s$ state and one electron each in the $2s$, $2p_x$, $2p_y$ and $2p_z$ states. These states would be observed in individual carbon atoms, not in solids where bonding results in the formation of energy bands. When the carbon atom is bound to four other atoms, for example 4 hydrogen atoms in methane, or four other carbon atoms in diamond, the energy states are slightly different. There are once again two electrons in the $1s$ state and four unpaired single electrons in the so called the sp^3 hybridized states. In the case of bonding in a molecule of ethylene, graphite or other carbon compounds having a $C=C$, one electron is left in a p_z state as in the single atom while the three other electrons occupy the sp^2 hybridized states. In the case of a molecule of acetylene or other molecules having $C\equiv C$ bonds, two electrons are left in the p_y , p_z states while two are in the sp states. The sp^3 hybridization in diamond fixes the direction of the bonds as 109° to each other. A model of the bonding in diamond is shown in Figure II.14. The resultant crystal cannot be easily deformed. This makes diamond the

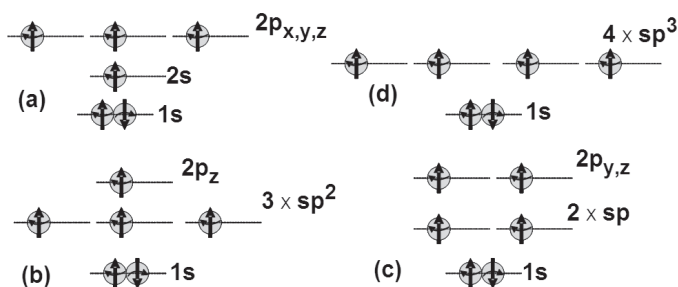


Fig. II. 13 Electronic energy levels of carbon atom in the atomic state (a), while bonded in graphite (b), acetylene(c) and diamond (d).

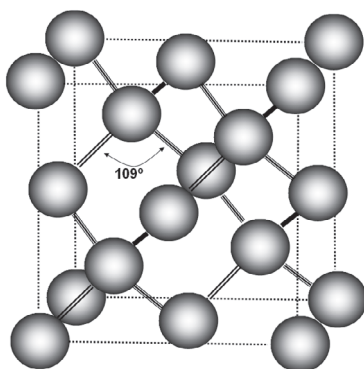


Fig. II. 14 The four bonds in diamond are oriented at 109° to one another.

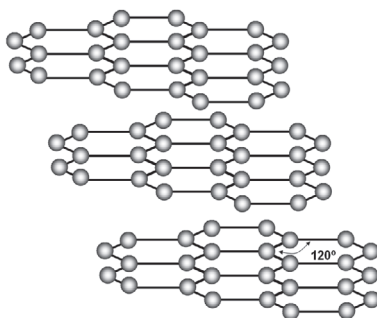


Fig. II. 15 Three bonds in graphite ring are in a plane at 120° to one another. Bonding between the layers is due to the 2p_z electrons.

hardest substance known. Similar covalent bonds directed in specific directions are present in ceramics such as titania, zirconia and alumina. These are strong materials since movement of dislocations in these lattices is very difficult. They are however very brittle for the same reason. The sp^2 hybridization of graphite provides three bonds which are at 120° to one another in a single plane. The bonding with the remaining p_z electron is of very low energy. This makes graphite a layered material that can be easily separated into thin flakes. Graphite conducts electricity and is used as a lubricant in some cases. A model of the bonding in graphite is shown in Figure II.15. The knowledge now permits the control of the relative concentration of the two types of bonding in a material and enables one to design a material with the desired properties. It is possible to deposit a thin film of a material which consists of a large number of small crystals of diamond connected together by small regions of graphite. The hardness of the material can be thus precisely controlled according to the need. Controlling the nature of chemical bonding in a material permits very precise control of the macroscopic or bulk properties of the material.

Precise knowledge of the bonding in carbon atoms also permits the design of other interesting materials such as carbon nanotubes, fullerenes or Buckyballs. Such structures are possible primarily because of the ability of carbon to form sp^3 , sp^2 and sp hybridizations which form the C-C, C=C and C \equiv C bonds. The same ability of the carbon atom is responsible for life. It is most likely that life in all parts of the universe would invariably be dependent on carbon. The carbon nanotubes and fullerenes can be considered as designed carbon molecules. As seen in figure II.16, a typical Bucky ball has 60 atoms of carbon and is often referred to as C_{60} . The structure resembles the geodesic dome originally suggested by Mr. Buckminster Fuller as the ideal structure to provide maximum space with minimum material. The later identification of these molecules once again emphasizes the ingenuity of nature in developing optimum structures.

Figure II.17 shows a carbon nanotube. Such molecules are the result of controlled joining of the graphite layers into well ordered three dimensional structures. A carbon nanotube is extremely strong. Including the nanotube into a composite results in an extremely strong

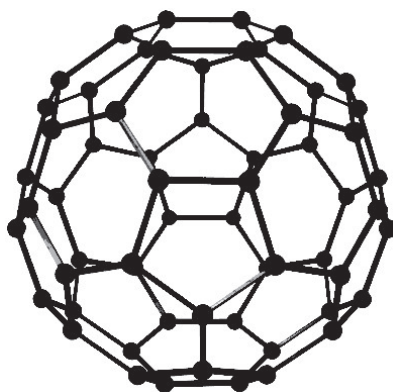


Fig. II. 16 A model of the fullerene molecule C_{60}

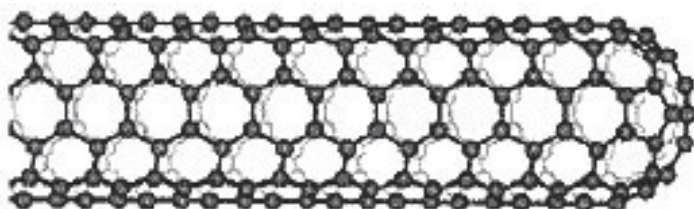


Fig. II. 17 A model of a carbon nanotube.

material. These carbon molecules, discovered only about twenty years ago are being investigated for a variety of other applications including catalysis, hydrogen gas storage and solar energy. Controlling the bonding in a material is a very powerful method for producing a material with desired properties. This may be considered as a case of molecular level design. However, another approach which is a true molecular level design is now a reality.

Designing the molecules

When we consider designing or producing a particular material to satisfy a particular need, one is coming very close to life. After all, life is the maintenance of an order, the order within the body which requires goal oriented action. Not surprisingly, living organisms offer

a wonderful example of molecular level design. The development of genetic engineering can be attributed to Francis Crick and James Watson (see the pictures in Figures II.18 and II.19) who finally confirmed the structure of the molecule of life deoxyribonucleic acid (DNA). They received the Nobel Prize in medicine for the year 1962 for this achievement. The design for the production of a material required for life, resides as a code in the genetic material DNA. The series of nucleotides on the twisted double helix of DNA contain the design information. A transcript of the information is first made in the RNA which is then used by the cell to form a protein which performs the basic biological processes of the living organism. Since the start of domestication of animals and later the development of agriculture, man has had the capacity to select the living organisms that best serve his needs. Selective breeding of the complete living organism has been practised for ten thousand years or more. It has been possible to selectively breed dogs for all kinds of uses from controlling sheep and guiding the blind to lap dogs for companionship. So far however, genetic information was not directly accessible. In the latest quest for molecular design of materials, this barrier has also been overcome.

Once again we can consider one example. It is known that the spider's silk is a marvel of nature. It is more elastic than rubber and



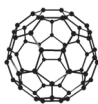
Fig. II. 18 Francis Harry Compton Crick



Fig. II. 19 James Dewey Watson

can be stretched by very large amounts without failure. At the same time, it is stronger than the equivalent thickness of steel! The earlier approach to develop a similar material would have been to examine the molecular structure of spider's silk. The constituent atoms could be identified and the nature of bonding determined. Attempts can be then made to duplicate the structure using advanced methods of chemistry and physics. This would be a "brute force" method based on systematic knowledge. A material called BioSteel, which has the properties of spider's silk, has been developed recently. However the approach is different. The gene responsible for producing spider's silk in the spider had been identified and transferred to a goat. The trans-genetic goat secretes the protein in the milk. The milk is processed to form Biosteel a filament of which is shown in Figure II.20 on colour plate vi (Page 10/11). A material with properties far superior to steel is thus produced for fabrication of small, precision components. This example of the technology developed by Nexia Biotech illustrates the beauty and elegance of the molecular design approach.

In the interests of providing a coherent easily accessible picture, the development of stronger materials from knowledge-based selection of naturally occurring materials to purpose-driven molecular design has been presented. Other examples can be identified in human cultural development. For example, one can consider the Stone Age iceman using naturally occurring birch polyporous, move to the trial and error approaches of Hypocrites, recognize the scientific approaches of Louis Pasteur and finally arrive at molecular design of medicines. The motive for describing this gradual development of human abilities is to create awareness of the ability of modern science as an overall framework of human understanding and communicate the excitement of the journey of man.



III Nanomaterials and Nanomachines

Nano in our experience

Human efforts to develop new materials have recently been helped by the technological ability to design and alter materials whose dimensions are in nanometers. These have been labeled as nanomaterials. Since the materials are three dimensional, obviously one can have one, two or all three dimensions of the materials being only several nanometers. Since typical inter-atomic distances are about 0.5 nm, each nano dimension can have between 5 and fifty atoms. A thin film or atomic layer of material has only one nano dimension. The two remaining dimensions are macroscopic. A typical real world experience would be a layer of oil on water which exhibits spectral colours when viewed in sun light. The thickness of such films must be comparable to the wavelength of light for interference effects to be observed. The study of thin films had been part of the semiconductor electronics industry for forty years. When a single dimension is considered to be macroscopic it is termed as a 1D material or a quantum wire. This description reflects the need to use quantum physics to understand the effect of having two nano dimensions. Good examples of common experience of a material with two nano dimensions would be spider's silk which is about 1000 nm in diameter. The technological capabilities have now enabled us to make long nano wires. When all three dimensions are in nanometers, the material is called a quantum dot or 0D material. A 0D material in common experience is the particle in a mist or fog. As in the case of interference from thin oil films, the scattering of light which results in fog is only possible if the particles are of a size

comparable to the wavelength of light, approximately 500 nanometers. Since the particles in fog also include a condensed layer of water, the dimension of the dust particle is a few nanometers. Obviously, since no dimension is macroscopic, individual 0D particles cannot be easily handled. So they are used either in powder form or scattered on the surface of macroscopic objects.

Is Nano really new?

While it is true that recent research efforts have been responsible for giving a wide publicity to nano materials, use of nanomaterials and their special properties can be traced back into the early part of human civilizations when trial and error approaches were made to develop new materials. The case of the Samurai swords has already been described. Repeated fold and forge technique has resulted in a material where the layer thickness is typically a few nano meters. A more exquisite example is the Lycurgus cup. One of the very unusual features of the Cup is its colour. When viewed in reflected light, for example in daylight, it appears green. However, when a light is transmitted through the glass, it appears red. This is shown in Figure III.1 on colour plate vii (Page24/25). Only a handful of ancient glasses showing this effect are known, all of them Roman. Modern investigations have revealed that this phenomenon is due to the precipitation of nanoparticles of gold in the glass. Like the Japanese artisans making the Samurai swords, the Roman glass makers of the 5th century AD had no idea of the concept of how the phenomenon was produced.

Commercial Nano Materials

Many uses of nanoparticles in current commercial products can be identified. Carbon filling of automobile tires provides maximum utility when the process is altered to ensure that carbon nano particles are present. Titania particles in high quality paints and thermal spray coatings are nano particles. Decorative coating and glazes on ceramic tiles and sanitary ware consist of nanoparticles incorporated into the surface of the ceramic. Catalysts have always been most efficient when used in a finely divided state. Most modern catalysts, including those used in automobile converters for pollution control, are nano

structured. The catalyst is divided into nanometer sized active regions. In many of these cases, the nano dimensions were not deliberately introduced. The materials were optimized for best performance. Subsequently it was identified that the best products contained nano particles. In contrast, use of nanometer sized components and layers in modern electronic devices has been deliberate. The increase in computer capabilities was achieved by integrating larger and larger number of transistors into a single integrated circuit or IC chip. Reducing the size of individual transistors and the distance between transistors increases the speed of operation of the IC. The dimensions of transistors in the most advanced IC's of today are 200-300nm. Correspondingly some of the films used in the fabrication of these devices are also very thin. The current devices use an SiO₂ layer only 70nm thick. Other commercial examples of nanomaterials which have now come into commercial use include silver bacterial wound dressings, conducting inks used for electronic packaging and structural polymer composites.

What makes nanomaterials so special?

The physics of nanomaterials can be discussed qualitatively to understand their potential. Atoms are typically about 0.2 nm in size and molecules are normally smaller than 1-2 nm. The physics of individual atoms and simple molecules can be understood by studying their interaction with electromagnetic radiation. This study, called spectroscopy, began with the original observation by Fraunhofer of the existence of atomic line spectra in the solar radiation. He found that the well defined colours emitted by atoms when heated to high temperatures, such as the yellow light of sodium, could be seen as dark lines in sun light. Such emission and absorption is observed when the individual atoms or molecules are isolated, like the molecules of a gas. The colours of light emitted by various elements can be quantitatively calculated using quantum mechanics. The first step in this direction was the determination of spectrum of hydrogen by Neils Bohr. This spectrum is experimentally observed only when hydrogen atoms are far apart and do not interact with each other. Liquid hydrogen obtained by cooling hydrogen gas to -252.8°C, does



Fig. III.1. The Lycurgus cup, a Roman artifact, more than 1500 years old appears green in reflected light and glows red in transmitted light. Modern science has established that this unique phenomenon is caused by the presence of nano particles of gold precipitated in glass. (The original piece of art is in the British Museum).

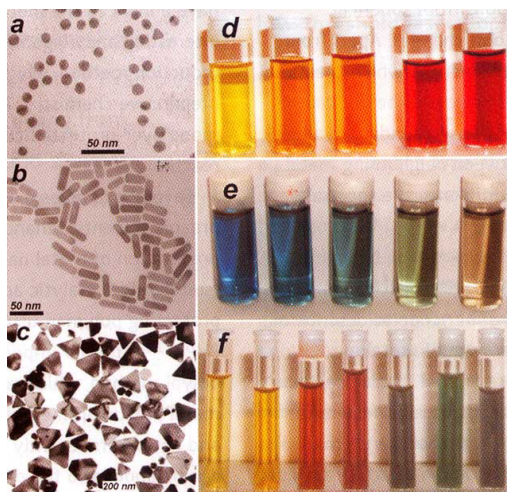


Fig. III.3 Transmission electron micrographs of Au nanospheres and nanorods (a,b) and Ag nanoprisms (c, mostly truncated triangles) Right: Photographs of colloidal dispersions of AuAg alloy nanoparticles with increasing Au concentration (d), Au nanorods of increasing aspect ratio (e), and Ag nanoprisms with increasing lateral size (f). (Reprinted with permission from Materials Today, 7, L M Liz-Marzan “Nanomaterials: Formation and colour” 26-31 © 2004 Elsevier).

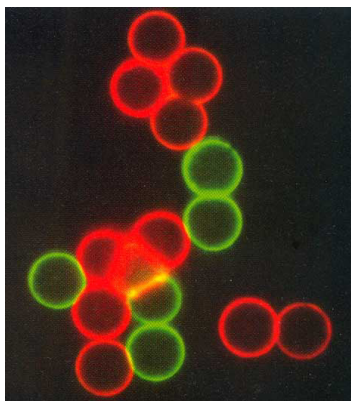


Fig. III.4 When coated on 5.2 micrometer size glass spheres, 2.5 nm CdTe nanocrystals emit green light while 4.4nm crystals emit red. (Reprinted with permission from Materials Today, 6, “Light manipulation” 7 © 2003 Elsevier).

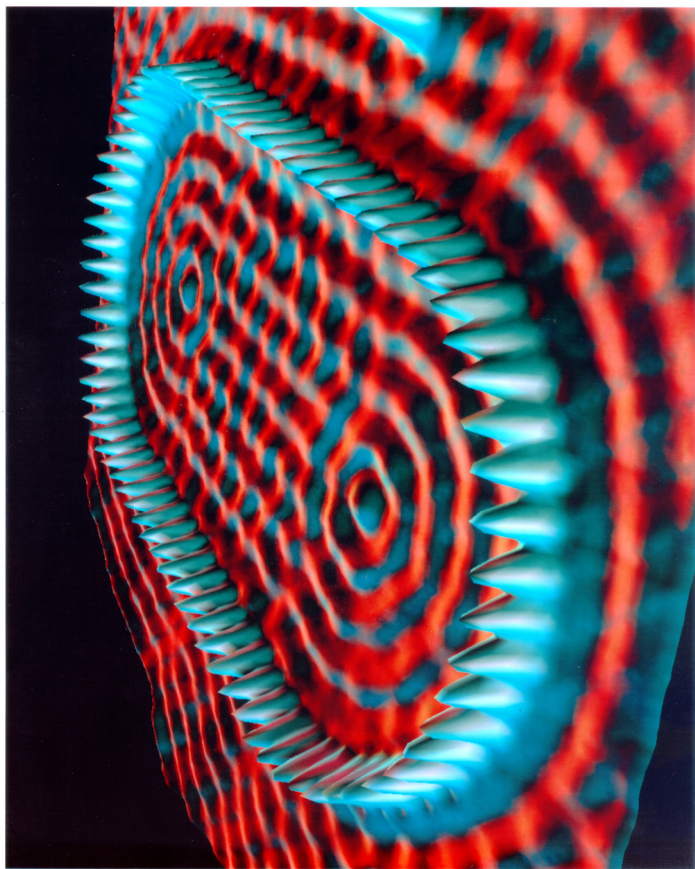
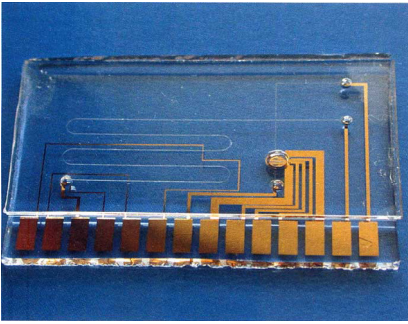
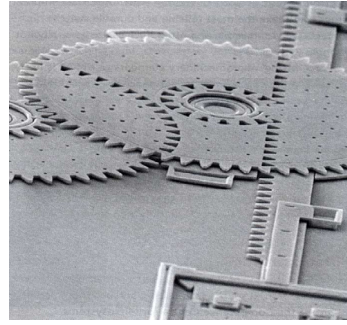


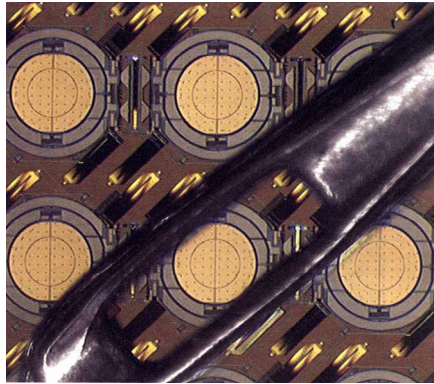
Fig. III. 13 “Stadium Corral” A series of iron atoms individually manipulated into place on a copper single crystal (reprinted with permission of IBM Corporation).



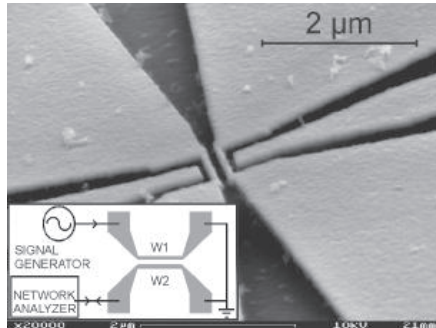
(1)



(2)



(3)



(4)

Fig. 111. 16 Examples of micro machines fabricated by lithographic methods. (1) A glass polymeric miniature chemistry lab, (2) silicon gear wheel, (3) hinged micro mirrors with electronic control Reprinted with permission from Materials Today, 5, G March “Micromachinery: Rolling at last?” 44- 49© 2002 Elsevier and (4) nanometer size mechanical resonator, reprinted with permission from Applied Physics Letters, 83, Laura Pescini, Heribert Lorenz, and Robert H. Blick “Mechanical gating of coupled nanoelectromechanical resonators operating at radio frequency”, 352 ©2003 AIP.

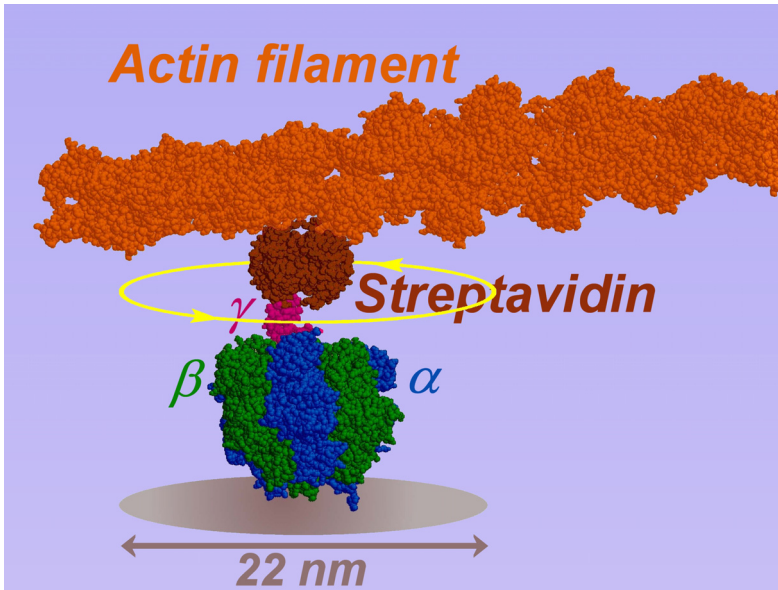


Fig. 111. 17 The ATPase molecule used to make a single molecule motor of 22nm size. (Used with permission of Prof. Kazuhiko Kinosita).

not exhibit the spectrum described by the Bohr model. This is not surprising since liquids are different from gases. The molecules of the liquid interact and this results in other interesting properties such as viscosity and surface tension.

When condensed matter (which includes both solids and liquids) is considered, interactions between molecules are very important. Many interesting properties are observed. Metallic luster, mechanical strength, viscosity, electrical conduction, ferromagnetism, superconductivity etc., are all properties exhibited by solids and liquids. Some of these, like ferromagnetism and superconductivity, can be explained only by quantum mechanical theory of interactions between atoms. In other cases, particularly for mechanical properties, it has not been possible to understand the properties in such detail. Thus systematic study shows that iron is a stronger metal than aluminum but it is not at all easy to relate that observation to the atomic properties of aluminum and iron. In contrast, iron is ferromagnetic due to interaction between electrons in the iron atoms.

In condensed matter, a number of atoms interact with each other. Typical inter atomic distance in condensed matter is 0.5 nm. As the size of the particles decreases, the number of surface atoms becomes a significant fraction of the total number of atoms. For a solid of 1cm^3 there are some 10^{22} atoms of which some 10^{15} are on the surface. For a solid 100nm^3 , out of the 10^9 atoms, more than 10^5 are on the surfaces. The ratio of surface to interior atoms increases by a factor of 1000. The variation of the percentage of surface atoms with the particle size is shown in Figure III.2. The surface environment is different. These atoms and molecules interact with much less number of molecules since one side of the surface atom is free. However, it is possible to consider that two or three layers of atoms constitute a surface. An atom in the second layer interacts with only one atom on one side but many more on the other. In such cases the percentage of surface atoms increases as shown in Figure III.2. If a single atomic layer is considered to be the surface, for a 5 nm particle, about 60% of the atoms are surface atoms. Since the inter-atomic distance is considered to be 0.5 nm, this is a cube of 10 atoms a side. Smaller particles would be better considered as individual molecules. If two

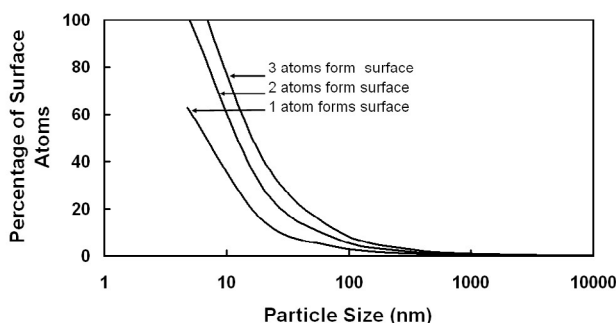


Fig. III.2 Variation of the percentage of surface atoms with the size of the particle

layers of atoms are considered as the surface, 30% of the atoms on the surface of a 20nm particle are surface atoms. If three layers are accepted, a similar particle would have nearly 40% of the atoms on the surface.

As mentioned above, all the interesting properties of solids and liquids are due to the interaction of the atoms and molecules. When the percentage of the surface atoms changes, the properties of condensed matter correspondingly vary. If a particular property is a consequence of the interaction of a large number of molecules or atoms, it is proper to consider that the surface consists of more than one layer of atoms. It is possible that for this property, three layers are to be considered to constitute the surface. As the particle size decreases below 200nm, the influence of surface atoms become significant and this particular property will change significantly. On the other hand, of for a different property, which involves interaction between much smaller number of molecules, it is perhaps more appropriate to consider the surface to consist of a single layer of atoms. Now significant property changes would be observed when the particle size decreases below 30-40 nm. These dimensions where significant changes in physical properties are observed are called “characteristic lengths”. These are usually in the range of 10-1000nm. This explains the excitement of nanomaterials. In nanomaterials, the dimensions are comparable with the “characteristic length”. Thus very large changes in the properties of materials are to be expected. A few

examples of characteristic length scales are shown in Table III.1. The specific value of the characteristic length also depends on the elements present, inter atomic forces and the structural arrangement.

Table III.1 Representative Examples of characteristic lengths

Electron wavelength	10-100nm	Electron Tunneling	1-10nm
Quantum well	1-100nm	Metallic skin depth	10-100nm
Magnetic domain wall	10-100nm	Dislocation interaction	1-1000nm
Catalytic surface	1-10nm	Grain boundaries	1-10 nm
Biopolymer secondary structure	1-10nm	Biopolymer tertiary structure	10-1000nm

Two types of properties are listed above. Dislocations and grain boundaries refer to structure of materials. A dislocation or a missing layer of atoms in the crystal lattice is responsible for easy deformation of materials. Normally a material consists of small crystals or crystallites which are also called grains. Grain boundaries which are 1-10nm thick separate the grains or crystallites. At these characteristic lengths, the mechanical properties of nano particles are significantly altered. Biopolymers, in particular proteins, are long chains of amino acid molecules. Typically more than 10,000 amino acids are joined to form a protein. This chain folds into a specific form called the secondary structure and a further specific form called the tertiary structure. Proteins act as catalysts. The secondary and tertiary structures are responsible for the catalytic action. These give rise to corresponding characteristic lengths as shown. In ordinary catalysts also the structure of the material in the length scale of 1-10 nm is important for proper functioning. Nanomaterials thus alter the catalytic action. Other characteristic lengths refer to quantum properties of materials. These are the reasons why 0D and 1D nanomaterials are called as quantum dots and quantum wires. Quantum mechanical tunneling is very important in several small transistors used in ICs. It is also responsible for radioactivity and is also exploited in the operation of a scanning tunneling microscope which enables “seeing the atoms”. Tunneling becomes important at 1-10nm. As the atoms interact with each other, the characteristic electron energy states

change. One example of this is the formation of C-C, C=C and C≡C bonds. In solids, when large number of atoms interact, these states change even more drastically. Instead of single levels, each of which contains two electrons, bands are formed. This band formation in metals causes electrical conduction. In semiconductors, small band gaps form. In nano materials, as the size is altered, it is possible to move from atom-like to bulk-like behavior. The particle may exhibit bands, like solid or single lines, like a molecule. Atom -like behavior in this context is called a quantum well. The corresponding characteristic lengths also are shown in Table III.1.

Demonstration Examples of the Nano phenomena

The dramatic influence of nano size on the properties of the material can be visualized by considering some very simple examples. The most basic property of a metal for example is its colour and luster. It is very difficult to confuse the yellow colour of gold with while colour of silver. However, high school chemistry offers a small clue. When silver is precipitated as small particles it appears black. Thus the colour and luster of silver are dependent on the particle size. The colour of silver nanoparticles depends most dramatically on the size and shape at nanometer scales as is visible in Figure III.3 on colour plate viii (Page24/25). Silver nano particles of different sizes and shapes are produced by controlled chemical methods. It is possible to form rods, spheres or pyramids. They are very small and do not settle as a precipitate. It is easy to note that as the particle size increases the colour of the particles shown suspended in water changes from yellow to red and finally to grey or black.

The colour of the silver nanoparticles is caused by scattering. In the case of semiconductors, the colour of light emitted due to exposure to ultra violet light changes. When electrons in the semiconductor are provided with high energy, by shining ultraviolet light on it, the electrons emit the energy back at the wavelength corresponding to the band gap of the semiconductor. Just as the colour of light emitted helped in the identification of elements, the colour of light emitted identifies the semiconductor. Typical examples of semiconductors which exhibit this phenomenon are compounds such as CdTe, CdS, ZnS and PbS. The optical emission of energy by the excited electron

is normally observed only in direct band gap semiconductors. Si which is an indirect band gap semiconductor does not normally show this behavior. In simple language, the electrons in Si when provided with a large amount of energy loose it in the form of heat absorbed by the solid rather than as emitted radiation. However, when silicon is finely subdivided into nanometer size wires it emits light. This is known as porous silicon. As the wire diameter is decreased, the emission shifts to blue colour from red. A similar result is obtained for all semiconductors. When nanocrystals of CdTe are formed and coated on glass spheres, the colour emitted is red for 4.4 nm crystals but green for 2.2nm crystals. This is shown in Figure III.4 on colour plate viii (Page24/25). When nano particles of the same size but of different compounds are considered, the colour emitted changes depending on the bulk property. The results for three similar compounds are shown in Table III. 2. The bulk band gap, which is a characteristic property, is measured in electron volts. One electron volt is the energy gained by one electron when it is attracted by a voltage of 1 V, a very small energy. Nanocrystals of materials with larger band gaps produce green or blue emission while low band gap materials emit red colour.

Table III. 2 Colour emitted by 4-6 nm semiconductor particles

Material	Bulk Bandgap (eV)	Colour Emitted
PbS	1.0	Red
CdS	2.5	Green
ZnS	3.5	White

The increase in efficiency of catalysts with reduced size is quite familiar. In school chemistry, finely divided Ni or Pt are mentioned as examples of catalysts. The catalyst does not participate in the reaction. It merely provides a site where the reactant molecules are temporarily bound till the reaction is complete. By using finely divided catalysts, the number of sites available for reaction increases and the catalyst becomes more useful. Another common example is the use of activated charcoal for the removal of foul odors from water and air. The activated charcoal has a large number of locations where the

unwanted molecules can get trapped. Sometimes the charcoal can be reactivated by heating, removing the trapped molecules. The shape of the active site in the catalyst is related to the shape and size of the reactant molecules trapped there. If the catalyst is a nanoparticle, it will be more easily accessible to the molecules in the gas phase. It will also be possible to have multiple catalysts each of which is fine tuned for a given reaction. Figure III.5 shows an example of a modern catalyst. Three different catalysts are employed. HCHO and CO are produced from more complex organic pollutants by the Pd-SnO₂ catalyst and from the nitrogen compounds by the Ir-La₂O₃ catalysts. The gold iron oxide combination oxidizes HCHO and CO to water and CO₂. Nano-sized structures increase the flexibility and permit complex reactions to be catalyzed. Japanese researchers have now produced such complex nanostructured catalysts with uniform particles smaller than 5 nm.

Another simple example for the relevance of particle size in the physical properties of materials is the use of particles and fibers for strengthening of materials, by preventing the movement of dislocations. The principle was discussed earlier. According to the experimentally confirmed Hall-Petch relation, if the grain size is reduced by a factor of 4, the strength increases by a factor of 2 (Square root of 4). This benefit is observed down to a diameter of 10-50nm below which the mechanical strength decreases. This is the

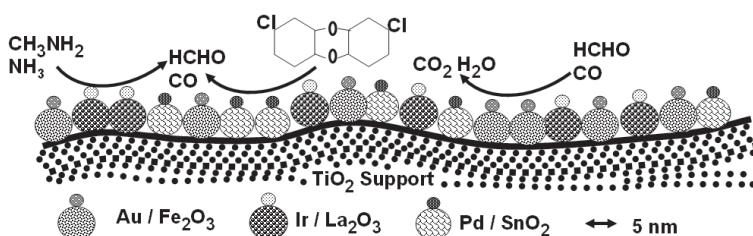


Fig. III.5 A schematic view of a catalyst using three different materials. Fine subdivision will enable better access of the reactant gases. The typical size of the particles can be as small as 5 nm in practice.

characteristic length scale. At smaller dimensions, a dislocation cannot exist and thus preventing its motion to increase strength is not possible. The simple examples, considered above, illustrate the relevance of the characteristic length in properties of nanomaterials.

Towards a bright future

Development of nanomaterials helps mankind move towards a bright future. The use of more efficient and better designed materials directly contributes to conservation of scarce natural resources. They offer more precise methods of addressing the problems of pollution and disease. The number of such applications, potential and actually commercialized, is very large. A few will be considered here.

Perhaps the most significant application of nanomaterials which has moved some distance towards commercialization is the use of nanoparticles of iron for cleaning ground water. Rapid industrialization, extensive use of pesticides in agriculture and increased human population have all contributed to the leaking of pesticide residues, nitrates, heavy metals such as Pb and organic molecules into ground water. It has been demonstrated that introducing nanoparticles of iron into the ground water upstream of the place where the ground water is being drawn for human consumption results in the precipitation of the impurities into insoluble iron complexes. Figure III.6 shows a schematic view of the approach. Using

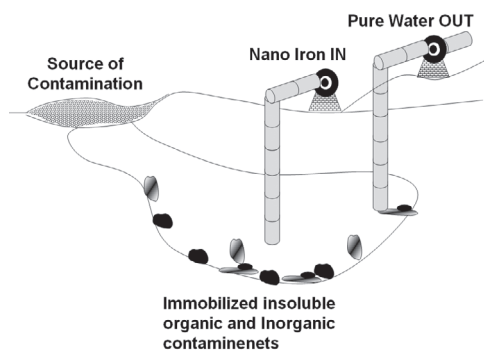


Fig. III. 6 Pumping of nano particles of iron upstream of actual use helps in purification of ground water

nanoparticles increases the reactivity. More pollutants would react with the nanoparticle. The use of a harmless material like iron reduces the chances of creating a new problem while solving an existing problem. Further the quantity of iron required would also be much smaller with the use of nanoparticles.

Hydrogen energy is a dream of the future. Burning hydrogen produces lots of energy, but does not lead to pollution since the only combustion product is water vapor. However, the current means of storing and transporting hydrogen are not safe and satisfactory. While some progress has been made in the use of metal hydrides, the compounds of metals and hydrogen, for the storage of hydrogen, filling carbon nanotubes with hydrogen is more attractive. The cheapest and most easily available material, carbon, can be used. Carbon nano tubes are formed by rolling and joining sheets of sp^2 bonded carbon. The same bonding as observed in graphite. Models of some of the carbon nanotubes that have been experimentally formed are shown in Figure III.7. Using precisely controlled chemical processes, it is possible to form carbon nano tubes with single, double or multiple layers. It is also possible to make a large single layer sheet of graphite and roll it up like a molecular sized carpet. Significant progress has been achieved in preparing large quantities of carbon nanotubes suitable for hydrogen storage. Lowering the cost of production is

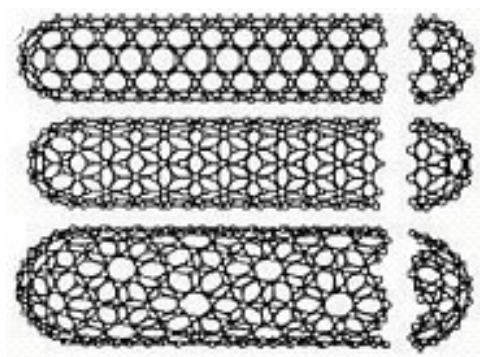


Fig. III. 7. Schematic pictures of some carbon nanotubes.

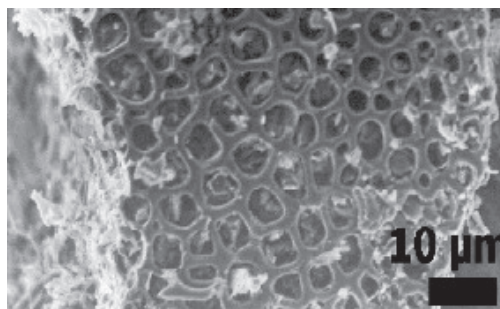


Fig. III.8. A scanning electron micrograph (SEM) of bundles of carbon nanotubes developed for hydrogen storage.

important since large quantities would be needed in the future. Figure III.8 shows an electron microscope picture of an array of carbon nanotubes specifically made for hydrogen storage.

Another exciting example involves the use of nanoparticles of Titania, a cheap material extensively used in the paint industry. By attaching proprietary catalytic molecules to the titania nanoparticles, a photo-assisted catalytic conversion of harmful atmospheric pollutants such as xylene and toluene into harmless products can be achieved. The porous nature of the Titania shown in Figure III.9 permits easy access to the gas molecules. It is being proposed to use the combination as a surface coating for roads to enable the immediate conversion of automobile exhausts.

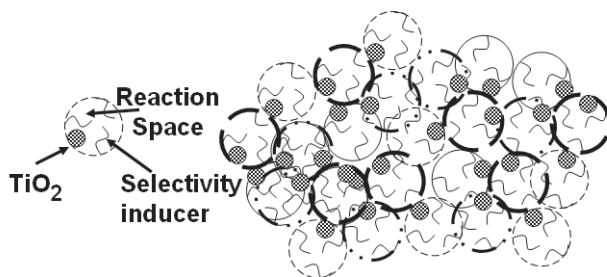


Fig. III. 9 A schematic view of a porous Titania material made of nanoparticles with active molecular attachments for photo catalysis

It has also been possible to assemble Titania nanoparticles into hollow micrometer size spheres. These spheres commercially labeled as TiNano® Spheres are excellent candidates for next generation medicine (drug) delivery. The small nanometer sized openings on the surface of the sphere permit controlled slow transfer of the drug held inside the sphere into the human body. While the drug delivery based on the TiNano sphere shown in Figure III.10 is a passive approach, a more active approach based on designer polymers is also being attempted.

Approximately spherical polymeric structures shown in Figure III.11 are made with designed nano cavities into which the drug molecules can be loaded. The surface of the polymeric sphere can be provided with specially designed protection polymers and also special recognizable organic groups. These are selected to bond specifically with a specific part of the human body, for example a cancerous tumor. The entire sphere would then move in the body until it attaches at the site of the tumor. The medicine loaded into the nano cavities will then be delivered locally to destroy the cancer cells and will not harm normal body tissue. The advantage of such a designed delivery is very obvious.

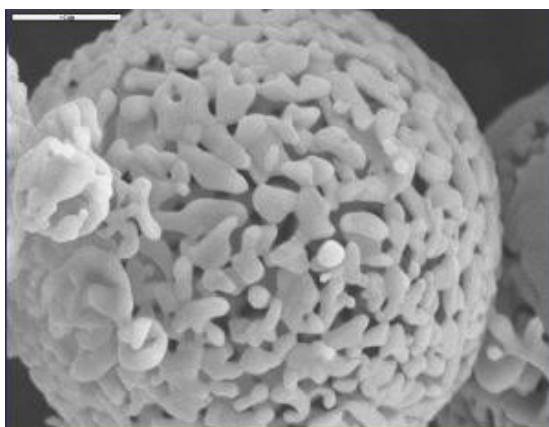


Fig. 111. 10. Spheres of titania nanoparticles Ti-nano® made for controlled drug delivery by Altair Nanomaterials Inc.

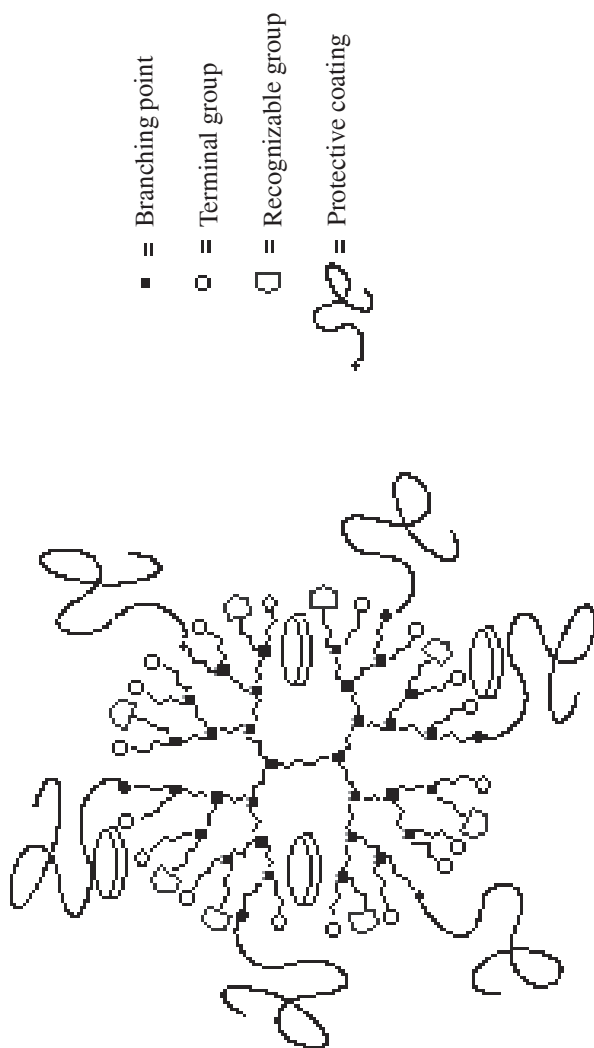


Fig. III. 11. Schematic view of a polymer nano sphere with nano cavities for drug storage. The drug molecules are shown as small disks. (Used with permission of Prof. Constantinos M. Paleos).

The above examples have been chosen from a very vast literature to highlight the exciting future possibilities. The ability to control processes and making newer nano materials is being improved continuously.

Nanotechnology and Nanomachines

The lecture by Richard Feynman to the American Physical Society in 1959 which he titled “There is plenty of space at the bottom” has been cited as a major turning point in the development of nanotechnology. Feynman, (see picture in Figure III.12) is more famous for the development of quantum electrodynamics, the theory of interaction of matter and radiation, for which he received the Nobel Prize in Physics in 1965. Basically the lecture pointed out that the principles of physics do not limit the sizes of machines and devices. Without violating the principles of physics it is possible to reduce the dimensions of a machine like an electric motor or the space required to write a quantity of information by several orders of magnitude. He offered personal prizes, \$1,000 to the first person who can take the information on the page of a book and put it on an area $1/25,000$ smaller in linear scale in such a manner that it can be read by an electron microscope and another \$1,000 to the first person who makes an operating electric motor smaller than $1/64$ inch cube. While the



Fig. III. 12. Richard P Feynman

motor was immediately built without any new technology, the prize for writing a page of the encyclopedia on the head of a pin was also claimed in Feynman's life time. The work of IBM group in manipulating individual atoms of iron on a single crystal of copper, perhaps achieves the ultimate limit in packing information. The picture in Figure III.13 on colour plate ix (Page24/25) has been named the quantum stadium. The surface is a single crystal of copper. Using a modified scanning tunneling microscope, single atoms of iron have been positioned in the shape of an oval. The wave like patterns noticed are the interference patterns produced due to the conducting electrons. Obviously it is possible to have an array of individual atoms. The presence of an atom can then be considered as a digit 1 and the absence digit 0. Thus we have the information regarding the presence or absence of atoms. The actual information required to be stored can be converted into a series of 0's and 1's using a code. Thus the position of individual atoms stores the information. Unless subatomic or electronic processes are employed, a single atom will be the smallest space in which information can be stored.

Making smaller and yet smaller objects has been continuously achieved in the electronics industry. The first transistor developed at the Bell laboratories in 1947 by Bardeen, Schokley and Brattain earned them a Nobel Prize in Physics in 1956. As shown in Figure III.14 , the first transistor was a single crystal germanium about 30mm in size. A latest transistor, a three gate device fabricated by Intel has features as small as 70 nm is also shown in Figure III.14. A typical integrated circuit currently is made of millions of devices; all fabricated using standard lithographic techniques. The decrease in device size is responsible for the calculating capability of computers which is doubling approximately every two years.

The lithographic process depends on materials called photoresists. A photoresist is a polymer which does not react with hydrofluoric acid and fluorine ions in gas phase. These react with silicon forming compounds soluble in water. Thus, when silicon is exposed to these chemicals or gases or ionized plasma, the silicon is removed or etched. The photoresist is applied on silicon so that this etching takes place only in some areas as required. It is difficult to apply a polymer on

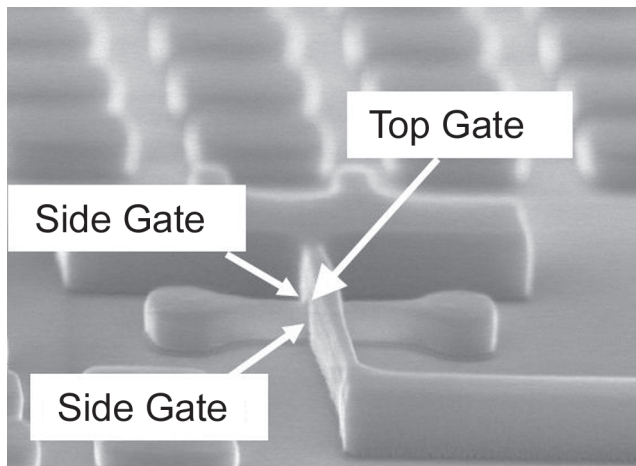


Fig. 111. 14 The first transistor made by Bardeen, Schokley and Brattain in 1947 at Bell Laboratories (top) compared with one of the smallest current devices, a tri gate transistor fabricated in 2004 by Intel Corporation (bottom).

selected regions particularly when these areas are very small. Thus resists are special polymers. A photoresist can be a monomer which is uniformly applied on silicon. Then some regions are exposed to either electrons or ultra violet light, where the monomer polymerizes. A solvent is used, which dissolves the monomer but not the polymer. This removes the photoresist in the regions where no exposure took place. When the fluorine based chemicals are used, silicon gets etched in the unexposed regions. In another type of photoresist, the polymer is applied. This polymer dissociates into monomers when exposed to UV or electrons. The solvent is once again used to remove the monomers. Now silicon is etched in the exposed regions. Continuous development of the lithographic process has ensured that smaller and smaller areas can be etched in a controlled way and smaller electronic devices can be made. The current sizes are as small as 70nm as shown in Figure III.14. Jack S Kilby (see Figure III.15) was awarded a Nobel Prize in physics in 2000 for contributing to the development of the first integrated circuit. The major attraction of the lithographic process is that a large number of devices can be made in one step. Modern IC's have millions of transistors due to the small size of the individual devices. Typically, on a six inch silicon wafer, hundreds or thousands of IC's can be fabricated together. The process can be

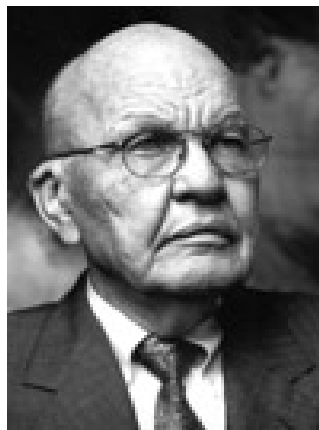


Fig. III. 15 Jack S. Kilby

automated. Thus in a modern silicon foundry, a place where these IC's are fabricated, millions of IC's can be fabricated with very little human intervention.

While the initial use of lithography was to develop smaller electronic devices, very soon it was realized that the same methods could be used to make small machines. As in the case of electronic devices, a large number of units can be made simultaneously, reducing the cost. Initially, the material used was only silicon and due to its superior properties, silicon is still preferred. However, other materials are also employed. Figure III.16 on colour plate x (Page 24/25) shows a series of examples. The first is a miniature chemistry laboratory fabricated out of polymers and glass. The fluid is moved in small capillaries some of which would be a few microns in diameter. The reaction vessels are very small, holding a micro liter or less of the reactants. Electrical measurements are used for quantitative analysis. A major advantage is the ability to handle very small quantities of very expensive chemicals or when very small quantities of material are actually available, as in crime detection. Another advantage is the ability to transport the chemistry lab as required. The second example is a small mechanical vibrator made of silicon. The small dimensions permit the natural frequency of vibration to be as high as 100 MHz. For comparison, the typical frequency of vibration of a macroscopic object, a bell or a string is typically only 100Hz. It is possible to electrically excite the mechanical oscillations in these silicon oscillators. These may replace the quartz oscillators being used currently. The third picture shows an array of small mirrors each of which is smaller than the eye of a sewing needle. These small mirrors are hinged. They can be electrically moved vertical to the plane of the paper. These arrays are used for routing the optical signals in telephone exchanges. Light gets reflected from a selected mirror which is moved into a vertical position into a particular direction onto a detector. The final picture shows some gear trains. These are typical mechanical devices very common in our experience, only very small. Wheels can be made mobile and free to rotate. They can be coupled electrically with miniature motors which are also made using similar lithographic techniques.

Physics in nanomachines

While the assertion of Feynman that physics permits the fabrication of nano machines is true, there are number of interesting novel aspects observed in such devices. The simplest machines are devices which permit the transfer of mechanical energy from one place to another. Thus simple machines include levers and pulleys. In most other advanced devices, a conversion of energy, usually electrical energy into mechanical energy is involved. The extremely small size of the nano machines means that the mechanical forces are also extremely small. The gravitational forces acting on these small structures are also very small. Thus, frictional, viscous and surface tension forces cannot be considered as a perturbation of the actual device performance. In many cases, these forces can be large enough not merely to prevent the optimum performance of the machine but to destroy the entire mechanical structure. While a large gear wheel can never be broken by viscous forces from the lubricating oil, a nanometer size silicon gear can very easily be shattered. Another major difference is the concept of pressure. Pressure is the average force transferred by molecular collisions. Normally this is a theoretical idea encountered in kinetic theory of gases and not a practical observable thing. The number of collisions of air molecules at atmospheric pressure is more than 10^{23} per square centimeter in one second. The average effect of these collisions is pressure. In these devices, the dimensions are comparable with the mean free path, the average distance traveled by a molecule before it collides with either the container or another molecule. The number of collisions is small. One cannot average molecular collisions into a pressure. The collision of a single air molecule to a nanometer sized gear or wheel transfers enough energy to move it. Since the numbers are small, the pressure would be felt as a series of individual collisions. Another major problem is the study of heat transfer. The thermal conductivity of a nano sized material is significantly different from the bulk value. This needs to be taken into account during design. The characteristic length scale introduced in the earlier section has to be considered. Many properties other than thermal conductivity could also change if the device dimensions are small enough. This makes the design of nanomachines a complex

issue and not merely reducing the sizes of the components. The famous biologist J B S Haldane once wrote an article explaining why an ant cannot be scaled up to the size of an elephant because the legs would need to be much stronger and why a whale can only survive in the sea where buoyancy reduces the gravitational force but not on the land. Similarly, the design of nanomachines needs a quantitative understanding of all the issues.

Learning from nature

Nature offers a wide variety of machines with capabilities far superior to the nano machines fabricated by lithography. Significant success has been achieved when simple approaches are borrowed from nature. The best example is the single molecule motor. This uses the functioning of the F1-ATPase molecule. The ATPase molecule is shown as a small ball below streptavidin molecule in Figure 17 on colour plate xi (Page 24/25). This is the most important biological molecule next only to the DNA. In nature, this molecule is found in all the cells of plants and animals. It is responsible for creating ATP with a very high efficiency. ATP is called the energy currency of cell since it provides the energy for all biochemical reactions. It has been possible to anchor the molecule on a glass and attach an actin filament as a spindle. When ATP is introduced, the spindle rotates using the energy from ATP. This is the smallest motor ever built. This was built not by designing every component from the molecular level but by using the capabilities available in nature.

The change in shape of muscles due to electrical energy is well known. This was the first observation of Alessandro Volta when he observed the movement of muscles of frog due to an applied voltage. At the molecular level the proteins have several possible secondary structures formed by folding of the protein in different ways. It is possible to make the protein molecule go into different shapes by using electrical energy. As shown in Figure III.18, a metal nanoparticle can be covalently bonded to a peptide chain. When electromagnetic energy is absorbed by the metal, the molecule could be switched to a different secondary structure caused by a different folding of the chain. The possibility of utilizing the single molecules of proteins for these

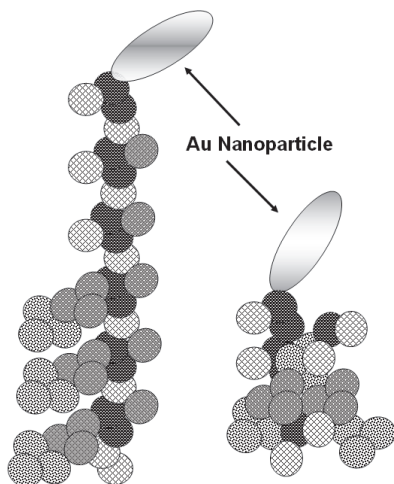


Fig. III. 18 Schematic picture showing the change in the secondary structure of a protein attached with a gold nanoparticle due to the absorption of electromagnetic energy by the metallic particle.

electronic and mechanical applications suggests that the use of biological processes for the production of technologically useful materials is very attractive.

Lithographic methods have the ability to produce large number of identical products. By reducing the minimum size of objects to a few hundred nm or less, it has been possible to produce millions of pieces in one step. This process is normally called a “top-down” approach since an initial large piece of silicon is subdivided by the process into a large number of units. In nature, there are many examples of products built of a large number of smaller units. A typical human body has about 10^{12-14} cells. These are however not formed by a “top-down” approach, but are formed by self organization. The subdivision of a single fertilized egg into the complete animal body is a complex process but it is not a matter of making a large number of identical cells. The more complex cells are made slowly from simple cells. This process is called the “bottom-up” approach of nature. This can be copied for the preparation of complex assembly of nanometer sized objects. The most interesting feature of self

organized assembly in living systems is the use of energetically weak bonds. The two strands of the DNA are bonded together by hydrogen bonds. The folding of the proteins is achieved by hydrogen bonds and Van der Waals forces. Since water is also hydrogen bonded, water serves sometimes as a mediator for forming hydrogen bonds in living organisms. Biological polymers are often made with one end being hydrophilic (attracting a water molecule), and the other end being hydrophobic (repelling a water molecule). This construction ensures that the repulsion and attraction among molecules results in the self organization of complex structures. The most important example is the formation of cell walls.

The complexity that emerges from self organization using such simple approaches is breath taking. Figure III.19 shows the levels of organization encountered in a single strand of hair. Even as simple a material as hair has as many as six levels of organization starting with a length scale of 0.15nm and ending with the overall hair diameter of 20 microns!

Experimentally, a few notable steps have been taken so far in producing nano materials by the bottom up approach. The simplest example, of the use of principles similar to those observed in living organisms, for the artificial formation of nanoparticles is “Strained Layer Epitaxy”. Normally when a thin film is deposited on a substrate,

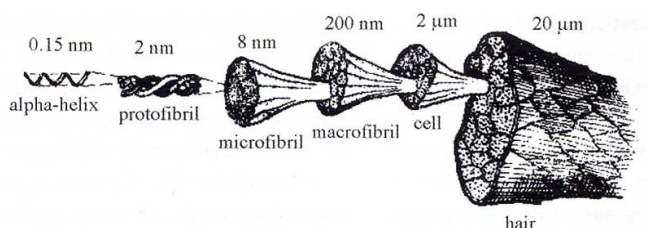


Fig. III. 19. The six levels of organization in hair starting with a length scale of 0.15 nm and ending with a 20 micron overall diameter. (Reprinted with permission from Materials Today, 5, J F V Vincent “Survival of the cheapest” 28-41© 2002 Elsevier.)

the crystals of the two materials need not have the same atomic sizes and arrangements. Sometimes the film deposited copies the structure of the substrate to minimize the repulsion between atoms. In other examples, the repulsion results in a strain between the film and the substrate. In a few cases the strain may be large enough to either cause the film to peel off from the substrate, or in rare cases, to even shatter the substrate. In a few cases however, the deposition conditions can be controlled in such a way that the deposited film collapses directly into a large number of nanometer size islands. Without the use of expensive lithographic processes, it becomes possible to form a large array of nanoparticles. An example is shown in Figure III.20. Quantum dots of a compound semiconductor, InP have been deposited on silicon substrate. The individual dots can be identified by the light emitted by them. There is, as of now, no capability of organizing such nanoparticles in regular pattern for technological use.

Recently, significant progress has also been achieved in developing artificial peptide chains which have well defined

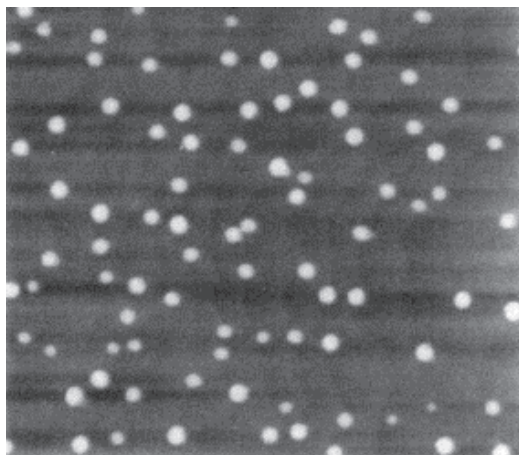


Fig. III. 20 Large number of semiconducting nanoparticles of InP formed by self organization following the deposition of a thin film. (Reprinted with permission from Materials Today, 6, D K Ferry and J P Bird "Transportation quantum dots"32-37 © 2003 Elsevier.)

hydrophobic and hydrophilic ends. In a water based solution, the hydrophobic ends form spherical micelles. This is similar to the action of soaps and detergents where the hydrophobic ends join together on the grease or dirt which permits the removal of dirt from the cloth along with the soap. It is possible to fine tune the repulsive and attractive forces and form multilayer structures in the form of spheres and tubes. In the case of a solvent other than water, the hydrophilic ends would be forced together. Representative examples of modeled structures are shown in Figure III.21. Formation of these structures has been confirmed for designed peptides such as V6D which use aspartic acid or lysine as heads with hydrophobic tails.

In nature, viruses have the ability to use the cell machinery for replicating their DNA. Essentially the virus uses the cell machinery to its own ends. Aping the virus, man has developed genetic engineering. So far, the approach has been to transfer genes from one species to another. This has resulted in such marvels as “bio-steel” described earlier, in which the protein for silk from a spider is transferred to a goat, or golden rice in which the gene for producing Vitamin A is transferred from daffodils to rice. Currently, efforts are being made for molecular design of artificial genes. This is based on

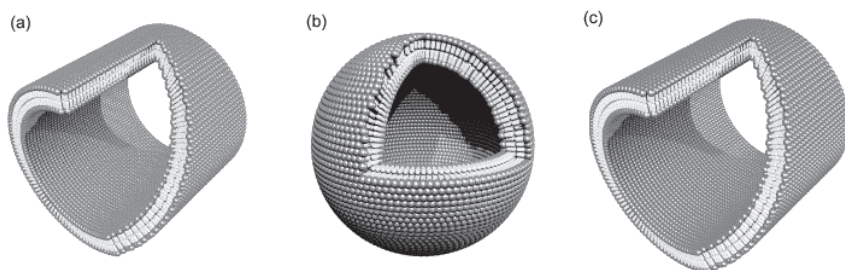
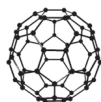


Fig. III. 21 Models of tubular and spherical structures formed with designer polymers with hydrophilic (dark) and hydrophobic (light) ends. (Reprinted with permission from Materials Today, 6, S. Zhang “Building from the bottom up ” 20-27© 2003 Elsevier.)

the modern technological ability to manipulate nanometer sized molecules. If the sequence of nucleotides is properly designed, a designer protein can be easily fabricated by exploiting the capabilities of the cellular processes. This will be the ultimate step in nanomaterial design. It will also be extremely powerful because only the design of the nucleotide sequence is necessary to produce the useful materials. Today we transfer the gene for making insulin required by diabetics, from one organism to another and extracting the insulin. In future it will be possible to design hormones more powerful than those available in nature and produce them in large quantities for human use. There is no limit in sight to the nano revolution. There is scope for participating in the quest and contributing for a bright future for mankind.



IV Concepts of Chemistry

Using chemical concepts

In the quest for newer and better materials, in the last two hundred years, science has provided major assistance. Science replaced the trial and error approaches used by humanity for developing materials such as bronze and iron which do not occur in nature. Though the trial and error methods had generated a large body of knowledge and experience, it is the scientific approach that has enabled us to improve the materials at a much faster rate. Experience is normally given a lot of credit. It is felt that experience even in the absence of any systematic scientific understanding should be the basis for acceptance. In the modern era, every failure is routinely attributed to the arrogance of science in neglecting “traditional experience”. The limitations of experience gained from trial and error were discussed briefly while describing the Delhi Iron Pillar. If at any time the artisan finds that the earlier achievements are not repeatable he is at a total loss, since he cannot have any means of isolating the cause and rectifying it. The number of things that can be changed is just too large for inspired guesses to work. Obviously, experience would help only when it is understandable and is integrated with the systematic knowledge of science. Experience cannot be a mystic ritual independent of systematic science.

The extensive knowledge particularly of chemistry accumulated over two hundred years is too large to be condensed here. Rather than attempt the impossible, this chapter provides a review of modern efforts at experimentally verifying the concepts used for creating the systematic study of materials. These recent experimental results reveal

the strength of these concepts of chemistry. Concepts such as atoms, molecules, valence, bond formation etc., form the core of chemistry which revolutionized materials development. However, these concepts were not directly introduced with the goal of developing new materials but were intended to explain the large number of systematic experimental observations. Systematic experimental study had revealed a large number of similarities that prompted these concepts.

For example, mercury, or quick silver as it was known, would become a white powder on heating in air with vastly different properties such as density, color and solubility. It could be recovered in the metallic form by further processing. Careful experiments showed that somehow the total quantity of the metal could be recovered. Further the weights of the metal and the oxide were always in a given ratio. Such examples make it necessary to classify materials into elements, compounds and mixtures. The concept that the elements were made of atoms and that small number of atoms join together in definite proportions to form compounds explained all the observations in a simple and elegant way. While atoms could not be observed, it was possible to demonstrate that an atom of carbon weighed as much as twelve atoms of hydrogen.

A number of other experiments were performed using electricity. Water is electrolyzed, converted into gases when electricity is passed through it. When a total charge of 96500 Coulombs is passed through the cell by placing two wires of platinum in water, the ratio of the weights of gases produced at the two electrodes would always be 8, and the ratio of their volumes would be 0.5. The volume of the gases would be multiples of 22.4 liters. One of the gases (hydrogen) is combustible and when it is burnt, water is produced and the weight of water produced is 9 times the weight of the gas. It is assumed that the experiment is performed at standard temperature and pressure (STP) which is conventionally an atmospheric pressure of 760mm of mercury column and a temperature of 0°C.

With such accurate experiments it has been possible to learn more details regarding the process by which atoms react with one another to form compounds. Water is a compound made up of molecules. It is

necessary to accept that at STP, 22.4 liters of any gas has 6.023×10^{23} molecules. This involves counting molecules present even when the molecules themselves are still hidden from view. Charge in multiples of $96500/6.023 \times 10^{23}$ Coulombs is exchanged during separation of a molecule of water. Thus the reaction of atoms is related with the exchange of charge. This can be considered as the first observation of the electron and determination of the electronic charge.

Further, systematic studies revealed more details of the reactions between atoms. As an example, Na_2O and MgO are compounds formed between similar metals Na and Mg with oxygen. Their properties are quite different. Na_2O is soluble in water while MgO is not. Clearly the electrons causing the bonding between Mg and O are behaving in a way different from the electrons that form the bond between Na and O. Concepts of ionic and covalent bond formation explain the difference between an ionic oxide like Na_2O and a covalent oxide like MgO . Thus the nature of the chemical bond was being more precisely defined.

Consider a few more examples. Copper is a metal which forms two oxides CuO and Cu_2O . In contrast, Na or Mg forms only one oxide. Helium does not form compounds. Such elements are called inert gases. Diamond and graphite involve bond formation between carbon atoms. It is difficult to visualize two materials which are more different in their properties. As attempts were made to understand the properties of the materials more accurately, it became necessary to consider the nature of electrons located in atoms. The concept of electron orbitals becomes essential to explain the chemical properties mentioned above.

So far the concepts of atoms, bond formation between atoms, causing the formation of chemical compounds and the existence of electronic orbitals in atoms are all indirectly supported by the observations of chemistry. In recent years, it has been possible to observe atoms, bonds and orbitals experimentally. These exciting results form the rest of the present chapter.

Observing atoms

Are atoms real or are they merely useful mental images which help

in understanding chemistry? If they are real, can they be actually observed? Such questions may now appear quite trivial. But fierce philosophical debates about the reality of atoms were common even upto 1900. Einstein showed that the motion of molecules of liquid would cause the random movement of micrometer sized particles suspended in the liquid. He calculated that the distances would be large enough to be observed in a microscope and that the measurement could also be used to experimentally determine the Avagadro number and the Boltzman constant. This theoretical development and the subsequent experimental confirmation by Perrin ended the philosophical debates. In the present context, the experimental results of Perrin were the first to directly visualize atoms and molecules. This however is still an indirect way. Rather than merely the number or the relative weight of atoms which could be inferred from quantitative chemistry, the kinetic energy of the molecules could be experimentally determined. Motion of small particles suspended in liquids, called Brownian motion, was observed seventy years before the theory of Einstein and there were speculations that the random movement was a reflection of the molecular motion. However the theory developed by Einstein and independently by Smoluchowski showed that the distance traveled by the particle undergoing Brownian motion varies as the square root of time. Perrin experimentally confirmed the square root dependence on time. One trace of Brownian motion obtained by him is shown in Figure IV.1. The distance traveled in successive intervals of time are in random directions and are of unequal length. However, the square of the net distance traveled, obtained by measuring the length from one point on the trace to another is proportional to the number of steps or points in between. The points are the observations of the position made after regular intervals of time. This type of movement is called a random walk. Since the direction is random, it would be thought that the particle should return to the original position. This does not happen because the probability of moving back in the direction from which it has initially moved is much smaller than moving in any one of the other directions available. Since the particle and the molecules of the liquid are at the same temperature, they have the same energy. The theory



Fig. IV. 1 Actual trace of a particle undergoing Brownian motion as determined by Perrin to verify the Einstein-Smoluchowski equations and reality of the atomic hypothesis

is also able to relate the distance traveled to the thermal energy of the molecules of the liquid and the number of molecules per unit volume. Perrin could calculate the average number of liquid molecules per unit volume using the quantitative theory. From this the Avogadro number could be determined. The particles exhibiting Brownian motion have a diameter 1000 times larger than that of the atom or molecule and could be observed in an optical microscope. Microscopically observing the atoms or molecules was not possible. Thus the experiments of Perrin were only indirect observations of the atoms. However, recent scientific developments have overcome this limitation and a direct observation of an atom is now possible.

The scanning tunneling microscope is the instrument which enables direct observation of atoms. To understand its operation, it is necessary to consider in detail the conduction of electricity through gases. A familiar example of such conduction is lightning. During lightning, electricity passes from one cloud to another or from a cloud to ground over a distance of several thousand meters. The voltage on the clouds increases gradually, due to atmospheric conditions, to more than ten thousand volts, due to the accumulation of charge. At this

point, conduction becomes possible over such distances. As the distance is very large, a very high voltage is needed to start the conduction. When conduction starts during lightening, the current could be as large as several million amperes. As soon as the charge available is exhausted, the current conduction and hence lightning stops. At a much smaller scale, this phenomenon is seen in arc welding which is routinely used for joining steel pieces, most commonly during building construction. Here, the distances between the two parts being welded is as small as a few millimeters. The current is a few amperes and voltages may be as low as a hundred volts. In the scanning tunneling microscope, the instrument used for observing atoms directly consists of a tip separated from the sample by a couple of nanometers. The current between the tip and the sample is maintained at the level of a few hundred picoamperes. The voltage is small, several volts. The distance between the two parts is a few nanometers.

Unlike the case of conduction in gases, where the gas molecules are ionized, movement of electrons, leading to the very low currents when the separation is a few nanometers is due to quantum mechanical tunneling. This quantum phenomenon which is most important for the operation of all advanced electronic devices is experimentally observed but, as with all quantum processes, its description seems to violates common sense. Imagine a large number of objects, let us say marbles placed in individual cups. Tunneling is a process whereby a few of the marbles would be observed to escape from one cup or the other without being raised above the rim of the cup! This never occurs in normal experience with large objects. In the case of small particles like the electrons, potential-wells, a small region in space with a lower potential energy, perform the same job as cups. Normally, energy would be required to move an electron to the top of the potential-well just as energy is required to move the marble to the top of the beaker. If the walls of the potential well are very thin, tunneling of electrons out of the well is actually observed. Surprisingly, not all electrons come out either. A small fraction of the available electrons tunnel out. This fraction can be calculated to a very high accuracy. In a scanning tunneling microscope, to generate the current of about 100 picoamperes, about a million electrons cross over the gap. The

voltage of a few volts is sufficient to attract a million electrons across a gap (or barrier) of a nanometer, but not for all the 10^{23} electrons present! The actual current is very critically dependent on the gap. Any small change in the gap leads to large change in the number of electrons. As the gap becomes larger, the number very soon becomes too small to be detected experimentally for such small voltages.

Consider the schematic representation shown in Figure IV.2. One part, which is shaped like a point is called the tip and it moves along the surface of the sample. Whenever the surface has a small depression, the current decreases since the gap effectively increases. Conversely, when there is small elevation, the current increases. (Assuming that the two do not touch and the gap becomes zero, in which case there is no tunneling). It is possible to use a feedback

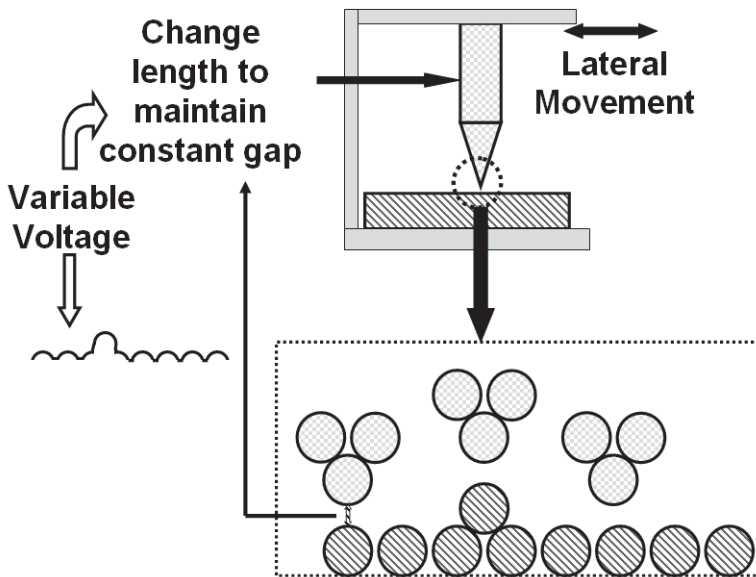


Fig. IV. 2 The principle of a scanning tunneling microscope. The tip moves over the sample. The variation of the applied voltage reflects the profile of the sample surface

mechanism to maintain the current. As the tip comes to a depression, the current decreases and the automatic circuit moves the tip down to maintain the current at a constant value. When it encounters an elevation, the tip is raised for the same reason. This movement of the tip is performed by a piezoelectric material. These materials contract and expand when an appropriate voltage is applied on them. This is similar to the expansion and contraction of materials with change in temperature. It takes a lot of time; tens of seconds for the temperature to increase uniformly to a new value, and for the length to increase, even for a good conductor like copper. The length of a piezoelectric material can be changed in microseconds by changing electrical voltages. The voltage applied to the material therefore is an indicator of the depressions and elevations in the sample over which the probe is moved horizontally on the surface of the sample. The resolution with which this can be done is so high that it is possible to actually create a map of the individual atoms on the sample surface.

Many advances in recent nano science and technology have been possible only because of the development of the STM. Gerd Binnig and Heinrich Rohrer (see pictures in Figures IV.3 and IV.4) were awarded the Nobel Prize for physics in 1986 for developing the STM. It has now been modified to actually move individual atoms from one place to another. Before the STM, was invented, the atomic



Fig. IV. 3 Gerd Binnig

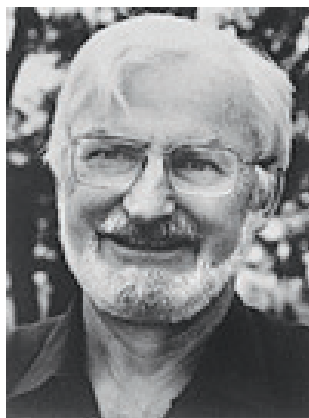


Fig. IV. 4 Heinrich Rohrer

arrangements of atoms were analyzed by X-ray and electron diffraction techniques. This worked only if the sample consists of periodic arrangement of atoms, when it becomes possible to calculate the intensity with which electrons or X-rays are scattered in any direction. By comparing with observations, it is possible to guess the arrangement of atoms. In contrast, the STM provides an image like an enlarged photograph in real space.

Figure IV.5 on colour plate xi (Page 54/55) shows representative examples of the results that can be obtained using the STM. Consider the arrangement of atoms of silicon on the surface of a silicon single crystal. This is not the arrangement of silicon atoms that would be observed inside the crystal or in the bulk. As with nanomaterials, the surface of silicon is altered due to the fact that there are no neighbors on one side of the surface atoms. The model of the surface of a Silicon single crystal obtained by heating it to very high temperatures in vacuum is shown in Figure IV.5. This model was originally developed by analyzing data from diffraction experiments. The atoms shown in red into the model can be clearly identified with the yellow orange circles into the STM image. The STM picture shown in Figure IV.5 confirms the model. Similarly the arrangement of carbon atoms in graphite can be seen in the STM picture of Figure IV.5. The six member model of the graphite ring has been superimposed in the STM image. The dark regions are the interior of the ring. The resemblance to the well known model of graphite is striking. Such experimental results have confirmed the atomic models developed nearly two hundred years earlier.

Observing the formation of chemical bonds

In the last few years, almost simultaneous with the ability to actually see atoms with an STM, it has been possible to experimentally confirm many of the other concepts of chemistry. This has been largely done using the techniques of femtochemistry. To actually follow the changes occurring in a molecule during the process of a chemical reaction is very difficult, since the measurement should not interfere with the changes occurring in the molecule. Obviously, it is not possible to catch one molecule and follow the changes occurring in it. It is preferable to detect a signal from large number of molecules.

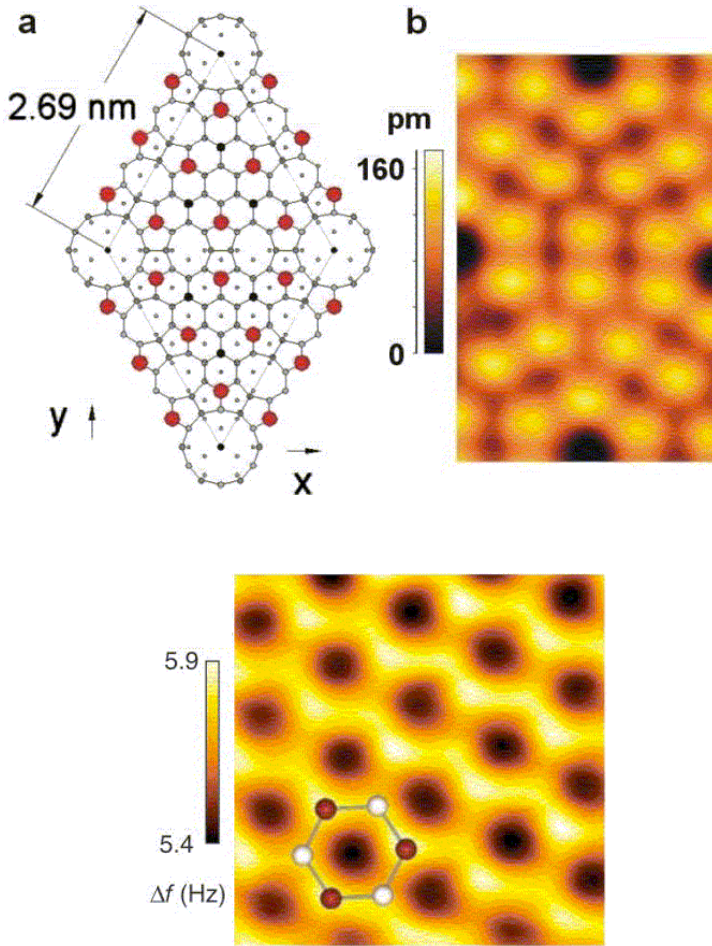


Fig. 4. V The model of reconstructed silicon surface STM image. (Reprinted with permission from *Physical Review B*, 68, M. Herz, F. J. Giessibl, and J. Mannhart, "Probing the shape of atoms in real space, 045301 © 2003 American Physical Society). The STM image of a graphite surface. (Reprinted with permission from *PNAS*, 100, Stefan Hembacher, Franz J. Giessibl, Jochen Mannhart, and Calvin F. Quate "Revealing the hidden atom in graphite by low-temperature atomic force microscopy" 12539, © 2003, The National Academy of Sciences USA).

Individual molecules are so small that monitoring the changes in a single molecule is very difficult even with the modern advanced methods. Since the molecules are identical, to monitor the changes occurring in a molecule during the chemical reaction, the reaction should start simultaneously in all of them. Otherwise it would be impossible to separate the changes occurring in different molecules. Finally the molecules are small objects which obey quantum mechanics. One strange quantum mechanical effect is tunneling. Another is interference. Particles obeying quantum mechanics can behave as waves resulting in constructive and destructive interference. The experimental conditions should be chosen to prevent quantum mechanical effects from obscuring the changes occurring within a molecule.

Recent work has shown that all these conditions can be met when a laser pulse of femtosecond duration is used to provide energy to a molecule. It is experimentally observed that all the molecules in the path of the femto second laser pulse absorb the energy simultaneously. Thus the change of state of all the molecules is synchronized. This is primarily because the typical time taken for any chemical reaction or rearrangement of electrons inside the molecules is a few picoseconds (10^{-12} s). This is significantly longer than the few femtoseconds (10^{-15} s) used for excitation. In all the molecules which have absorbed the energy, the electronic changes such as bond breaking, forming etc.,



Fig. IV. 6 Ahmed H. Zewail

occur together. This solves one of the problems mentioned above, since the reactions in all molecules caused by the input of energy will begin simultaneously. It is possible to use a second femtosecond pulse of laser to probe the condition of the molecule. Pulses of the second (the probe pulse) laser are delayed with respect to the first pulse which is called the pump laser pulse. The delay between the pump and probe pulses is experimentally varied. The response of the molecule to the probe pulse provides information about the state of the molecule at the time of the probe pulse. Thus, the state of the molecule after a small time interval from the start of the reaction is determined. By repeating the process with different delay times, the changes in the molecule occurring during the few picoseconds of the chemical reaction can be determined. The alteration of the state of the molecule due to the probe pulse is not relevant. The experiment is terminated with the probe pulse and repeated again with a new pump pulse and a new delay time. The use of femtosecond laser pulses also avoids the problem of quantum mechanical interference. The distance traveled by a molecule during this time period is so small that such effects become negligible. The elegance and power of the technique developed by him earned Ahmad H Zewail, (See picture in figure IV.6) a Nobel Prize in Chemistry in 1999.

The typical femtochemistry experiment is conducted using a molecular beam. The molecules being investigated are made to enter an ultra high vacuum chamber. The design of the chamber shown in Figure IV.7 ensures that all the molecules are traveling parallel to

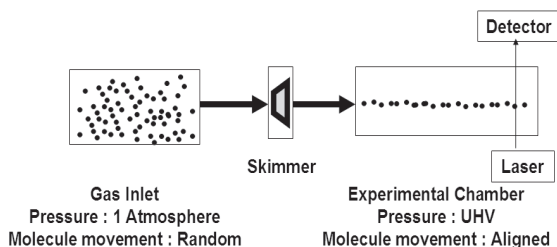


Fig. IV. 7 The schematic of the basic femtochemistry experimental setup. The Skimmer is designed to provide an aligned beam of molecules in the UHV chamber.

one another and perpendicular to the path of the laser. The skim-mer is designed to ensure that while the molecules in the chamber at atmospheric pressure travel in all random directions, the molecules in the beam in the ultra high vacuum experimental chamber are closely aligned to one another.

The schematic of the pump-probe system is shown in Figure IV.8. The laser pulses are directed to the chamber by reflection from a number of mirrors and prisms. A series of electronically controlled mirrors are used to provide an extra time delay for the probe pulse. This is easily done, since the distance between the mirrors can be altered. This ensures that the light beam for the probe pulse has to travel an extra distance and will arrive at the chamber later. The velocity of light is extremely large, 300,000 km/s and thus an extra distance of 3 microns will mean a delay of 10 femtoseconds. These distances are easily controlled using modern electronic controllers. The pump probe takes a more direct path and reaches the molecules first. In practice the electronic and optical control of these experiments are extremely complex.

Experiments performed with femtosecond laser pulses permit the study of chemical reactions and changes occurring within the

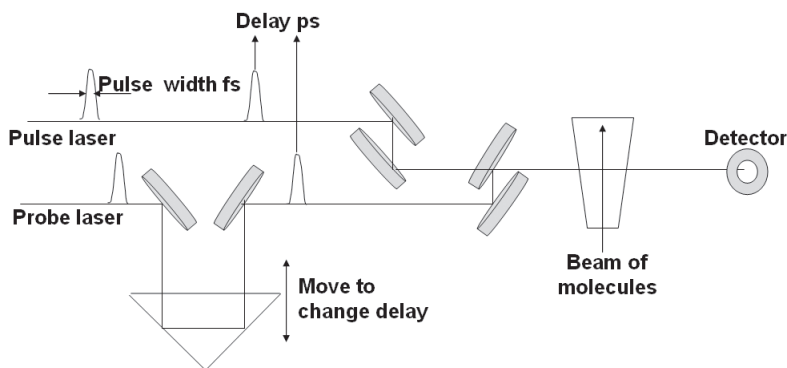


Fig. IV. 8 A schematic view of the pump and probe laser pulses in a femtochemistry experiment

molecules. Thus, instead of observing the atoms constituting a solid, after the bond formation between atoms has been completed, the actual formation and breaking of chemical bonds can be observed. The experiments performed on Sodium Iodide (NaI), illustrate the capabilities of this procedure. Theoretical work has shown that the ionic bond forms in NaI when the inter-atomic distance is 0.35 nm. At this distance, there are eight electrons with the Iodine nucleus, one more than the seven present in an iodine atom. The sodium atom has one electron less. This leads to the formation of Na^+I^- . The theory suggests that a covalent bond formed between Na and I atoms when the electrons would be shared, would be of higher energy, except when the inter-atomic distance is more than 0.7nm. This theoretical picture is shown in Figure IV.9. Since physical systems prefer the lower energy states, when the atoms are separated by 0.35nm, the ions should form. If they are at distances larger than 0.7nm a covalent bond should form. The response of the molecule to the probe pulse can confirm the actual state of the molecule. When a molecule of NaI dissociates, it would be expected that the bond would be transformed, from an ionic bond to a covalent bond, as the distance between the two atoms increases, before the molecule finally breaks and the two atoms are separated. In the actual experiment, the probe pulse detects

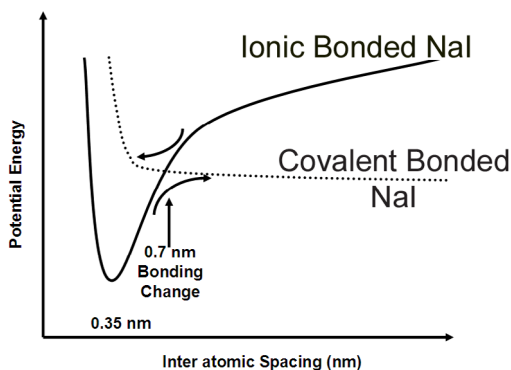


Fig. IV. 9 Variation of the energy of ionic and covalent bonds between Na and I atoms as a function of the inter-atomic distance.

a resonating behavior of the molecule. The results are shown in Figure IV.10. The molecule vibrates as if the bond is really a spring with the inter-atomic distance first increasing and then decreasing several times before the molecule is broken. Further, the bond characteristic does convert to the covalent form as the separation increases beyond 0.7nm, as predicted by the theory. When the molecule vibrates, the ionic bond converts to covalent when the distance increases. The reverse happens as the distance decreases again. The experimental confirmation of the formation of various types of bonds is one of the important scientific achievements of recent times.

Femtochemistry techniques are able to monitor changes in the molecule very closely. As another example, consider the dissociation of cyclobutane into two molecules of ethylene. Figure IV.11 describes the dissociation expected from the fundamentals of chemistry. As the molecule absorbs energy, it becomes highly energetic. Such high energy molecules, which exist for such a small time duration, are called transient states. Experimentally, it is observed that this proceeds through two steps. Initially, one bond between carbons is broken. This breaks the square ring in the cyclobutane molecule. This molecule exists for a few hundred femtoseconds. Then the second carbon-carbon bond breaks and the two molecules of ethylene separate.

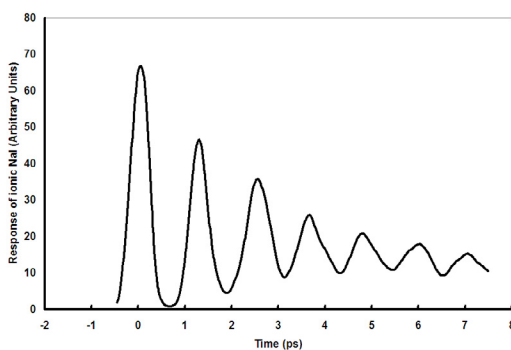


Fig. IV. 10 Response of Ionic bonded NaI to the probe pulse reflecting the number of such atoms existing at a given time after the pump pulse has energized the molecule.

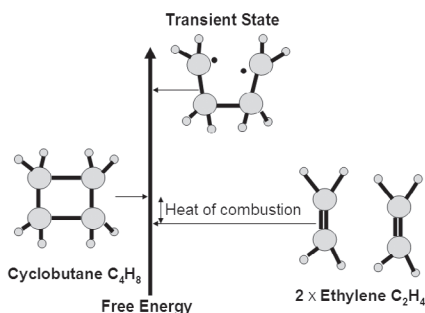


Fig. IV. 11 Experimentally confirmed picture of the dissociation of cyclobutane molecule with the formation of a transient state.

Femtochemistry allows detailed observation of the transient state and process whereby the molecule is broken. The experiments also confirm the higher potential energy of the activated transient state.

Femtochemistry has been a very successful approach for understanding the properties of individual molecules with the resolution to actually identify the changes occurring in specific bonds. A great example has been the visualization of the electronic charge transfer occurring in the molecule of chlorophyll. As with all biological molecules, chlorophyll is a large complex polymer. Sunlight provides energy to several bonds in the molecule of chlorophyll. This energy is finally used to produce ATP which is then used by the leaf to produce molecules of carbohydrates from carbon dioxide. Using the techniques of femtochemistry, it has been possible to monitor the transfer of the energy within the molecule from one location to another within the molecule, to know the sequence of absorption of light at various points and to provide a description of the various steps in photosynthesis, from the absorption of the photon to the final use of this energy for the creation of ATP.

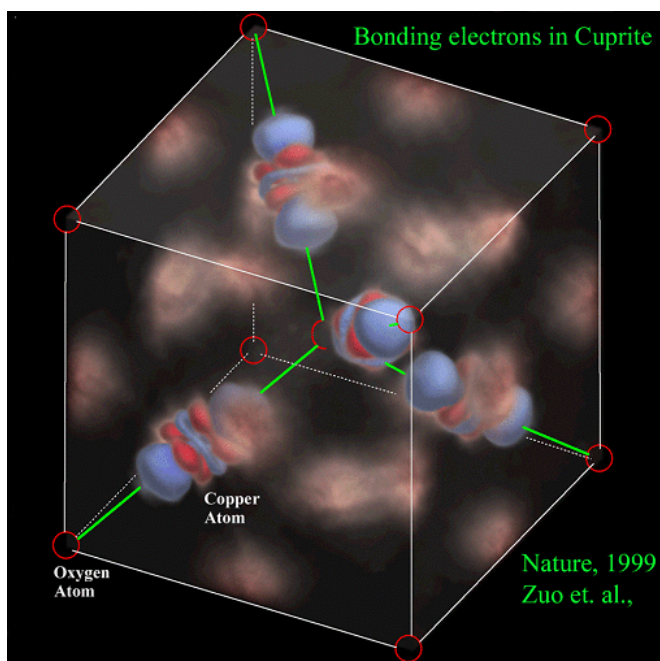
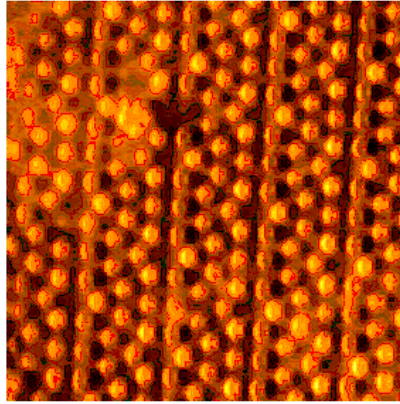
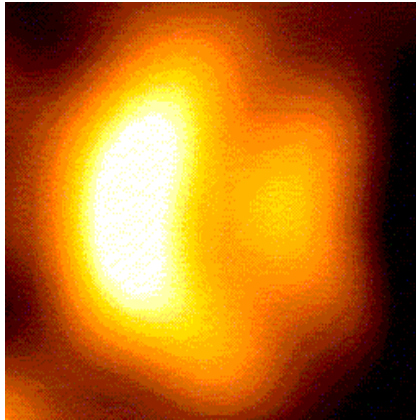


Fig. IV. 12 Electron density at copper atom determined by diffraction experiments (Reprinted with permission from Nature 401, J M Zuo, M Kim, M O’Keeffe and J C H Spence “Direct observation of d-orbital holes and Cu-Cu bonding in Cu_2O ”, 49- 52, © 1999 Nature Publishing Group).



(a)



(b)

Fig. I V. 13 The STM image of the reconstructed Silicon surface (a) has been determined with sufficient accuracy to reveal in the picture of the individual atom (b), the differences in electronic concentration caused by the orbitals of silicon. (Reprinted with permission from Science, 289, F J Giessibl, S Hembacher Bielefeldt and J Mannhart, "Sub atomic features in the Si (111) (7X7) surface observed by atomic force microscopy", 422, © 2000 The American Association for the Advancement of Science).

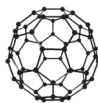
Observing the electrons in chemical bonds

The concept of observing an electron is controversial. Electrons obey quantum mechanics. They exhibit behavior which cannot be visualized in terms of simple macroscopic objects such as particles and waves. Quantum mechanics simply provides a theory which enables us to calculate the probability for detecting the electron at a particular place. The probability for finding an electron is high over a small region of space which is termed as an orbital. [In technical language, this is just the shape of the function $\psi\psi^*$ where ψ is the wave function obtained in quantum mechanics as a solution to the Schrödinger wave equation.] It can be argued that the orbital is really a mathematical and probabilistic concept that cannot in principle be observed. However, electron density at different points in a real crystal can be determined experimentally using X-ray or electron diffraction. Using extremely precise diffraction experiments it has been possible to determine the electron density at the site of a copper atom in a crystal accurately enough to confirm that the shape of the electron density distribution in space is exactly identical to the theoretical predictions. The picture in Figure IV.12 on colour plate xiii (Page60/61) shows the region near the copper atoms where electrons are located. The shape resembles a dumb-bell with a doughnut located at the neck of the dumb-bell. This is the shape of the $d_{x^2-y^2}$ orbital. Given that quantum theory has now been confirmed to an accuracy of one part in several billion this is perhaps only to be expected. Nonetheless, the image produced by experiment of the d orbitals of copper is a wonderful expression of experimental capability.

Diffraction is not the only means of observing electrons present in chemical bonds. Recent work with the scanning tunneling microscope has also been successful in achieving such resolutions. The tunneling of electrons between the tip and the sample is dependent ultimately on the electron density. The shape of the atom observed is really the shape of the electron cloud. The nucleus is in any case too small to be observed. An atom is nothing but the region around the nucleus which contains the electrons. An STM picture obtained for the surface of single crystal silicon is shown in Figure IV.13 shown on colour plate xiii (Page60/61). The resolution of the instrument

has been enhanced by special methods. The STM picture shows two maxima which have been shown separately in detail. It is known that Silicon atom forms four bonds with sp^3 orbitals oriented at 109° with respect to each other. It has been possible to confirm that the two maxima observed are caused by the presence of two bonds formed in different directions.

Interestingly using STM, it has been possible to confirm that under certain conditions, a temporary bond forms between the tip and the sample. When this bond breaks, energy is lost. This is the first time a purely mechanical phenomenon of energy loss, (friction) could be precisely and quantitatively coupled to the basic chemical process of bond formation. The recent past has enabled experimental confirmation of the concepts used by chemists to systematize the experimental observations. This strengthens the confidence in experimental science. The search for materials has now gone much beyond systematic study to designer materials and emulating nature. The basic concepts however continue to be important in conceptualizing and planning future developments. Designing molecules has to take into consideration the reality of the concepts of potential barriers, atomic orbitals and nature of chemical bonds. Nature has, in the course of organic evolution, built up the complexity within these constraints of physics and chemistry.





V Probing Matter

The logic of probing matter

In the quest for new materials, chemistry provides crucial assistance. Chemistry has made it possible to systematically search for new elements, determine new means of producing valuable metals and lower the cost of producing materials. In the process, trial and error approaches were replaced by systematic understanding. Chemistry has been helped by microscopic techniques of analysis. Any report of the development of exciting new materials comes with the mention of a large number of modern techniques used to determine the properties of materials at the atomic level. These techniques helped to build atomic scale models of the material. These models provided a more precise understanding of the materials than was possible with the concepts of bonding and chemical reactions. Starting with the development of the optical microscope nearly two hundred years ago, a number of experimental techniques have been developed. Newer instruments continue to be developed every day. The present effort seeks to explore some basic principles involved in analyzing materials at the atomic level.

The necessity for atomic level understanding of materials becomes apparent when the properties of iron are considered as an example. Iron has been the most important metal responsible for the spread of human culture. Being easily available, iron has been used for producing the tools required for agricultural implements for more than 3000 years. It is an early experimentally observed fact that iron can be hardened by controlled heating, also called tempering. While chemical tests confirm that iron is an element, elementary chemistry

fails to explain the reasons for the hardening of iron. Similarly, elementary atomic theory considers the formation of molecules which are formed by a small number of atoms reacting together in fixed proportions. The formation of metallic alloys seems to violate the idea of molecular formation. Alloys can be formed over a continuously variable range of compositions.

Consider the addition of carbon to iron. That this lowers the melting temperature of iron was known from ancient times. But the mechanical properties of iron-carbon alloy vary in a complex way with the addition of carbon. Considering the small quantities of carbon used, usually less than 1-2%, the formation of molecules based on the reaction of iron and carbon atoms does not seem to be possible. The role of a small quantity of carbon in altering the mechanical properties of iron and steel cannot be explained by elementary chemistry. Consider further, the addition of a small quantity, once again a few parts per hundred, of chromium to convert iron into stainless steel. The steel becomes non-magnetic, it does not rust easily and is also stronger than iron.

It is clear that understanding the properties of materials involves concepts beyond those of elementary chemistry. It is necessary to experimentally investigate the materials and probe the neighborhood of the atoms. The symmetrical order exhibited by the packing of the atoms into a solid has to be determined. It is necessary to identify the atoms present without ignoring the traces of impurities which are capable of significantly altering the properties. It is necessary to identify the bond formation taking place locally and finally to understand the arrangements of the atoms leading to the bulk material.

In order to probe the immediate environment of an atom, we need probes which are small compared to the size of the atom. Thus matter can only be probed using electrons and photons. Actually neutrons are also used and in certain circumstances they offer some special advantages. However, producing and handling neutrons is very complex and so using neutrons in laboratories is not very common. The present discussion concentrates only on how photons and electrons can be used to probe matter and answer the type of questions raised earlier.

The probes: Electrons and photons

Electrons are normally visualized as small particles revolving around the nucleus which has protons and neutrons, like some kind of a miniature solar system. Maxwell had shown that light is an electromagnetic radiation; a wave like the water waves. Varying electric and magnetic fields are found in the light waves in the place of moving water surface. Electromagnetic waves have been shown to have a wavelength, the distance between two successive crests of the wave, ranging from 0.1nm for X-rays to several meters for radio waves used for radio transmission. Quantum mechanics has shown that to explain all observations, electrons and photons (particles which form the electromagnetic wave) have to be considered as quantum objects and not as small particles or waves. The photon of an electromagnetic wave of wavelength λ behaves sometimes like a particle of energy hc/λ where c is the velocity of light and h is the Planck's constant. An electron traveling with a velocity v also exhibits wave properties with a wavelength of h/mv which is called the de Broglie wavelength. The values of the wave length of electron and energy of Photons are a tabulated in Table V.1. The small value of the Planks constant h ensures that these quantum features are not perceived by our senses. This limits the quantum paradoxes, which violate common sense, to the physics laboratory.

In probing matter the approach is to strike the material under investigation with electrons or photons and observe the consequent changes. To understand this logically, it is useful to compare the energy and wavelength to the properties of atoms and materials. Bohr's model of the hydrogen atom shows that the energy of the electron in the hydrogen atom is -13.6 eV. For other atoms this energy is multiplied by the atomic number. The energy required to form a chemical bond or create a defect in a material is approximately 1 eV. Similarly 0.1 eV of energy would set a bond into vibration just like the vibration of a string of a violin. In terms of dimensions the size of typical atom is 0.1 nm, the inter-atomic distance in a molecule is 0.5 nm and a typical grain in a solid substance is about 1000nm in size.

Table V.1 Energy and wavelength values for electrons and photons

Electron Energy(eV)	de Broglie Wavelength(nm)	Photon Wavelength(nm)	Photon Energy(eV)
1	1.23	0.01	124k
10	0.39	0.1	12.4k
100	.123	1	1.24k
1k	.039	10	124
10k	.0123	100	12.4
100k	.0039	1000	1.24
1M	.001	10000	0.124

The scattering of electrons and photons from materials is fundamentally no different from the collision of ordinary objects. When two steel balls collide, the collision is for all practical purposes elastic. Kinetic energy can be transferred from one ball to another, but since the steel ball does not deform easily and is normally very smooth, there is almost no loss of energy as heat. On the other hand, one can consider collisions between easily deformed rubber balls where some of the energy is converted into heat. These are called inelastic collisions.

Probing matter with electrons and photons involves either elastic or inelastic collisions. When elastic collisions take place, the electrons or photons used as the probe do not loose any energy. Thus, the angle through which they are scattered and the intensity of the scattered radiation provide information regarding the material. During inelastic scattering, the energy of the incoming particle changes. Except in a few cases, the energy is transferred to the material being probed resulting in the emission of either electrons or photons of lower energy, which can be detected. These detected particles provide a wealth of information regarding the material. Different combinations lead to a number of techniques useful for probing the materials.

Elastic scattering of electrons and photons is the basis for optical microscopy, electron microscopy, X-ray diffraction and electron diffraction. If interference takes place between waves scattered from different parts of the sample, diffraction is observed. If scattering

from individual parts of the material is detected without interference, microscopy is performed. The smallest parts of the material that can be seen in microscopy are those comparable in size to the wavelength of the incident particles.

During inelastic scattering of electrons, Auger electron spectroscopy detects low energy electrons and energy dispersive X-ray analysis is performed by detecting the photons. When photons are inelastically scattered from matter, during photoelectron spectroscopy, electrons are detected. In Raman Spectroscopy photons of wavelength different from the incident photons provide the relevant information. These are some of the most important techniques for probing matter. Others which cannot be placed in this simple classification scheme are not considered here. These include magnetic resonance, positron annihilation and mass spectroscopy.

While the principles involved in probing matter can be qualitatively discussed as above, the actual experiments can be performed only for limited ranges of wavelengths and energies of the particles. Microscopy can be easily performed using visible light. This is because in the human eye, one has a very useful detector. Microscopes using UV radiation are never built. Not only is it difficult to find materials for the lenses, at the end a complex mechanism would be needed to either photograph the object or convert the UV signal into visible light. As the energy of the electron is reduced to nearly 1eV, performing any experiment becomes very difficult. Similarly when we use extremely long wavelength photons, the energy is too small for any interaction with the material under test. At the other end of the spectrum, a very high energy photon such as a gamma ray does not interact with material. A very high energy electron beam would damage the material, rather than help in studying its properties. For these and other reasons, the selection of the energy range of the electrons and photons for a specific investigation technique is quite limited.

Another issue to be considered is the interaction volume and penetration depth. If we consider the simple case of visible photons, light can penetrate more than a few feet in glass but would not

Table V.2 Important techniques used for probing matter

Technique	Probe	Detection	Application
Low Energy Electron diffraction (LEED)	Electrons of energy less than 100 eV	Interference between scattered electrons	Surface Structure
Auger electron Spectroscopy (AES)	Electrons with ~1KeV energy	Detect electrons created by Auger process	Surface composition and bonding
Selected area electron diffraction (SAED) in transmission electron microscopy	Electrons with 20-100 KeV energy	Interference between scattered electrons	Structure of samples less than 100nm in thickness
Scanning electron microscopy(SEM)	Electrons with 20-100 KeV energy	Scattered electrons from features smaller than wavelength	Surface features
Energy dispersive averaged X-ray analysis (EDAX)	Electrons with 20-100 KeV energy	X-rays generated by electrons	Composition over the penetration depth of electrons
X-Ray Diffraction (XRD)	X-rays of wavelength ~01.nm	Interference between scattered X-rays	Bulk structure
X-ray photoelectron spectroscopy (XPS)	X-rays of wavelength ~1nm	Electrons generated by photoemission	Surface composition and bonding
Ultraviolet photoelectron spectroscopy (UPS)	UV radiation of wavelength ~10nm	Electrons generated by photoemission	Surface composition and bonding
Optical microscopy	Visible light	Scattered light from features smaller than wavelength	Surface features
Raman Spectroscopy	Visible light	Light of a different wavelength	Bonding between atoms

penetrate 100nm of silver film, which makes a glass mirror completely reflecting. Silicon would transmit IR radiation but not visible light. This behavior is related to the bandgap of the material. Photons of energy smaller than the band gap get transmitted. At high energies, wavelengths less than 10nm, photons are always transmitted since the energy is much larger than any possible bandgap. However, it is noticed that the penetration is less for materials with high atomic number. Lead is a good barrier for X-rays but not aluminum. Thus when a photon is used to probe the material, the photon energy and the properties of the material decide whether the bulk or the surface properties are determined. X-ray diffraction would give details of the bulk order of the material but optical microscopy would provide information only about the surface.

The penetration of electrons is dependent in a more complex way on the properties of the materials. As an approximation, it can be accepted that electrons of energy less than 100eV can only be used for probing the surface structure. 1 keV electrons can penetrate upto about 30nm. The penetration of electrons increases to about 5000nm for 50KeV energy. However, this penetration involves significant loss of the energy. Electrons generated by Auger or photoelectron emission have an energy less than 1 KeV. However, electrons which help in identifying the atoms and bonding are useful only if they have originated from the top 3nm of the material when the energy loss is very small. This is called the information depth for these techniques. In contrast, X-rays generated deep in the material can be detected easily providing information about the bulk composition. When transmitted electrons are detected for microscopy or diffraction, the sample must be thinner than about 100nm. When scattered off the surface, the electrons can provide information of the surface structure averaged over a small depth depending in a complex way on the material and the experimental setup. Table V.2 summarizes these discussions. Using a few examples, the principles involved in these methods of probing matter are now discussed individually

Techniques of microscopy

Microscopy, whether optical or electron, is fundamentally similar to

visual observation. Radiation scattered from an object is converted into a two dimensional picture on a photograph or a television screen just as in the eye. In normal vision, the resolution is limited to an object of about 0.1mm. This is the limitation imposed by the lens in the human eye and the response of the retina. This is significantly larger than the wavelength of visible light which is about 500 nm. Theoretically, the size of an object that can be seen with light of a particular wavelength will be slightly larger than the wavelength. This limitation is called the Raleigh criterion. When we consider the intensity of light reflected from a rectangular object, the intensity profile is not a rectangle. The diffraction or bending of light at the sharp edge is possible when the wavelength is comparable to the dimension of the object. Such a process is the reason sound can be heard around a corner; since the wavelength of sound is comparable to the dimensions of rooms and walls. The intensity of light from a small hole or source of dimension comparable to the wavelength of light will consist of a central maximum followed by one or more small peaks around it. A circular hole will show up as a central bright spot with a couple of weak rings around it. Obviously if two holes are close together they may appear as a single hole. The limit is defined to be the distance when the central maximum of one falls on the first smaller peak of the other. Figure V.1 shows the merging of two peaks

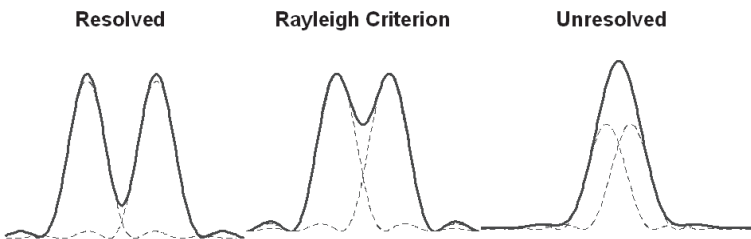


Fig.V. 1. Raleigh criterion. Features nearer than this criterion cannot be distinguished thus limiting the magnification that can be achieved.

of diffracted radiation emerging from two holes separated by a very small distance, as the holes come close to one another. When the separation is larger than the Raleigh criterion, the two can be easily distinguished. From the quantitative theory of diffraction it can be shown that the limiting dimension will be comparable to the wavelength. Since the wavelength of visible light is 500nm, it might appear that an optical microscope can be used to visualize objects as small as a 1000nm. Such magnifications are very difficult in practice. The reason for this is a problem common to every photographer: depth of focus. Basically a focused beam of light is a cone. The object is not an absolutely flat surface. When one part of the sample is brought sharply into focus, the beam of light or electrons is of the smallest size. This is shown in Figure V.2. Parts of the sample which are either at a larger or a smaller distance to the lens have a spot which is much larger. They are out of focus. The parts of the sample which are at the correct distance are clearly seen while the other regions cannot be seen clearly. It will be necessary to decrease the aperture or reduce the magnification to bring these areas into focus. This practical problem due to the sample, limits the magnification that can be actually realized in a microscope.

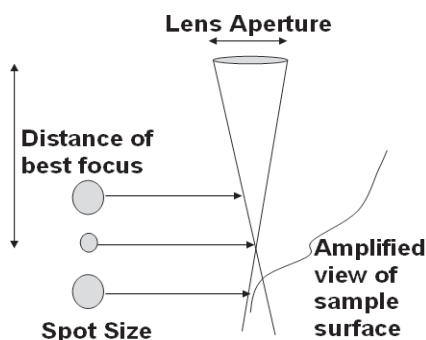


Fig. V.2 The diameter of the focused beam becomes larger for sample features at distances smaller or larger than the optimum distance from the lens thus limiting the practical magnification.

Both optical and electron microscopes can operate in a transmission or surface scan modes. Obviously transmission is only possible if the thickness of the sample is very small. Students of biology can be often frustrated when the section turns out to be too thick and nothing is visible in the microscope. When a sample thickness is reduced, it is most important to ensure that the sample is not damaged in the process. This is most often a problem for using a TEM with bulk samples which have to be reduced to about 100nm for meaningful pictures to be obtained. Reducing the thickness of a bulk sample to such dimensions can cause changes in the sample. In a scanning or reflection mode, it is easier to prepare the sample since only the surface is to be polished. However, even this has to be performed very carefully to avoid damaging the sample. The depth of focus limits the magnifications obtained in all cases. The magnifications achieved using electron microscopy could be as large as 300,000. This permits direct observation of nanometer sized objects. Ernst Ruska was awarded a Nobel Prize in Physics in 1986, for his contribution towards the development of an electron microscope (see picture in Figure V.3) However, it is not possible to observe individual atoms except under some very rare occasions. Microscopes are more flexible than the STM discussed earlier. It is easier to observe a sample at different magnifications. This compensates for their lower magnification.

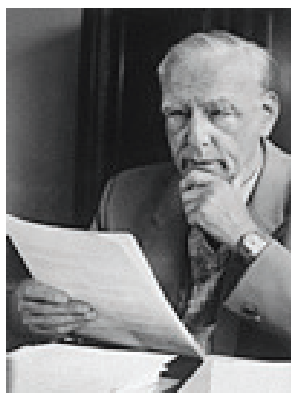
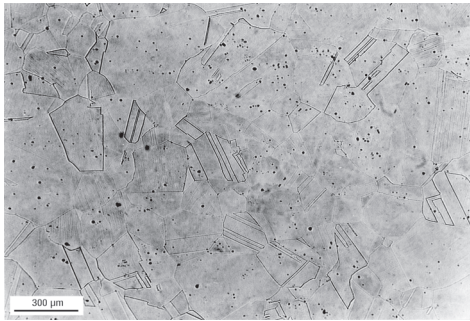


Fig. V.3 Ernst Ruska

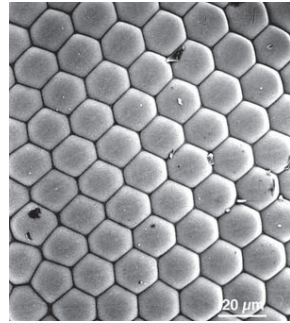
Figure V.4 shows some representative examples of the results obtained from microscopic examination of materials. The optical micrograph shows large austenite grains in a sample of steel. The sample has to be polished to a high degree to achieve the kind of surface required to achieve high magnifications particularly in the reflection geometry. At the same time care has to be taken to ensure that the grains are not deformed by this polishing. Any deformation would obviously make the micrograph useless. A second example shown in Figure V.4 is the scanning electron micrograph of a biological sample; the array of hexagons forming the composite eye of a moth, taken with a magnification of 550. Such samples cannot be polished. As the surface is not a plane, clarity is lost at the edges of the picture due to the curvature of the sample. Depth of focus has become an issue even though a magnification of 550 is very small compared to the capabilities of an electron microscope. The globular heads and 50 nm long tails of small proteins can be clearly distinguished in the next picture demonstrating the ability of a TEM to resolve features as small as several nm. Under ideal conditions, the TEM can be used to resolve individual atoms. The final micrograph shows individual gold atoms. This picture was taken by the FEI Company as a demonstration of the capabilities of their instrument. The arrows point to three different grains. In this sample, the grain boundaries, introduced earlier, can be identified as the lines along which the order in the arrangement of atoms changes direction. Grain boundaries in steel shown in the optical micrograph have the same property but the boundaries are not so perfect.

Diffraction Methods

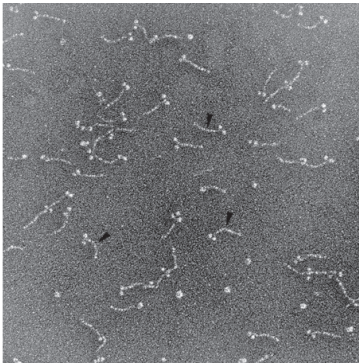
Elastic scattering of electrons and photons is used for evaluating microscopic order in the sample by operating in the Fourier or reciprocal space. Fourier or reciprocal space is a mathematical construction which enables the visualization of order in the material. It is experimentally linked to the intensity of radiation diffracted from the sample. Through a mathematical calculation which has become extremely easy due to the use of a computer, the diffracted intensity is converted into a description of the order or symmetry with which atoms are arranged to form a macroscopic solid. The mathematical



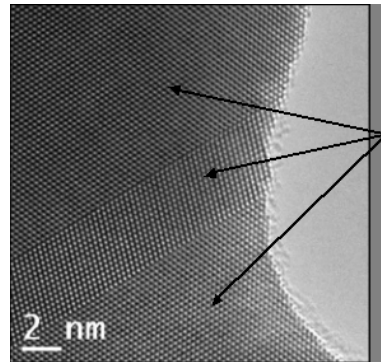
(a)



(b)



(c)



(d)

Fig. V. 4 (a) Optical micrograph of steel showing large austenite grains. (Used with permission of Prof. Simon Ringer.) (b) SEM of a moth's eye (X550) (c) TEM of proteins showing globular heads linked to a tail, 50-100 nm long. (d) TEM of a gold film showing individual gold atoms demonstrates the capabilities of the instrument developed by FEI Inc.

idea of Fourier, developed initially to solve problems of heat flow in materials, is that any repeatable function of any shape can be decomposed mathematically into a summation of a series of sinusoidal functions. The frequencies of the various components will be multiples of a basic frequency. The amplitudes and phases can be adjusted to obtain a proper fit with the original shape.

The easiest way to visualize this is to consider a simple square wave as in figure V.5. A single sine wave of equal frequency is obviously a poor approximation to the square wave. If another sine wave with three times the original frequency is added the approximation looks good if the amplitudes are properly chosen. By adding waves with further multiples, five and seven times the frequency and so on; it is possible to make the combination identical to the original square wave. The great insight of Fourier was that this is true for any function. To achieve a greater accuracy, it is necessary to add higher frequencies. The amplitudes and frequencies can be

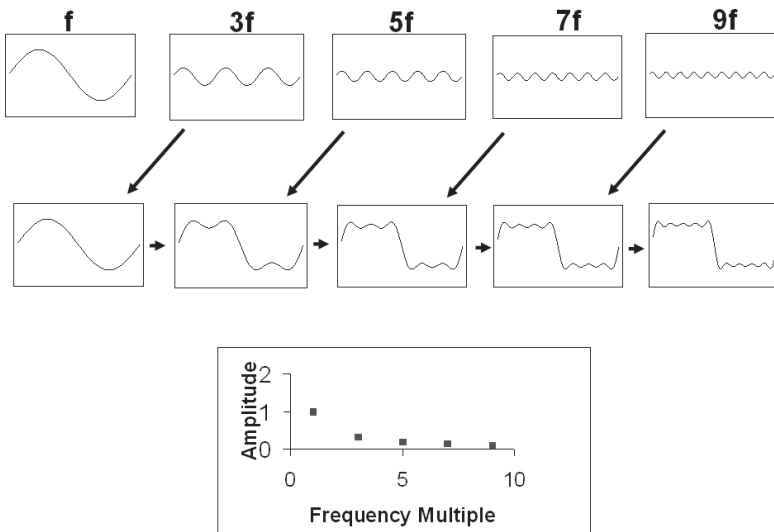


Fig. V.5 The principle of the Fourier summation. As components with odd multiples of frequency are added, a close approximation to a square wave is realized.

shown in a separate figure which has all the information required to calculate the original function. The mathematical processes of decomposition and reconstruction are called Fourier and inverse Fourier transforms respectively.

The simplest way to recognize the relation between this mathematics and reality is to look at the intensity of light emerging from a rectangular slit and the Fourier transform of a single rectangular shape. Both are identical and are mathematically called the sinc functions. This similarity is illustrated in Figure V.6. At the left of the picture the mathematical transformation of a square wave is shown. At the right, the light is shown falling on a slit. The slit is a rectangular hole in a screen. At the slit, light intensity will be zero where the light is blocked and a constant non-zero value where the slit is open. Thus the intensity of light at the slit is a rectangle. The intensity of the diffracted light is the sinc function in both cases, as shown. The diffracted intensity has the information required to determine the order in the shape of the slit. The shape of the slit can be calculated mathematically from the amplitude of the diffracted light. This diffraction intensity function was used to define the Raleigh criterion earlier.

Atoms interact and form liquids and solids. In an ideal solid, the atoms are arranged in a regular order. In a solid, since the atoms are

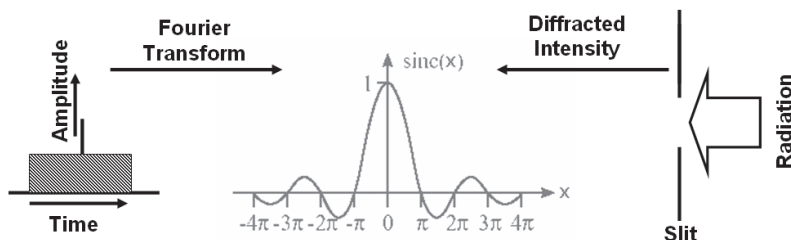


Fig. V. 6 The mathematical correspondence between the intensity of radiation diffracted by a rectangular slit and the Fourier transform of a rectangular shape.

close together, it is energetically preferable to arrange them in an order so that the attractive and repulsive forces balance exactly. If both attraction and repulsion between the like and unlike charges did not exist, no solid can exist. Without repulsion, atoms would all go to a single point. Without attraction they would all fly apart like a gas. In a real solid, when there is an order, the electron density is also periodic. Electron density is simply the amount of electronic charge per unit volume present at a given location. This periodic electron density can be decomposed into its Fourier components and this is nothing but the intensity of radiation diffracted from the material. The only requirement is that the experiment should be so arranged that the radiation scattered from the various atoms should interfere. Then in principle it is possible to calculate the pattern into which electrons and X-rays would be diffracted from a possible order of the atoms in the crystal. This calculated intensity can be compared to the experimentally observed intensity. The order assumed for calculation can be modified till it matches the experimental results. Thus the order inside a solid can be determined by diffraction methods. In practice, it is not very easy. The model has to be guessed based on past experience and then the scattered intensity calculated. Then, it is possible to determine the order inside a solid quite accurately. Since the wave lengths of only electrons and X-rays are of atomic dimensions, these are used to determine the order.

The best example of the success of the approach is the ability to determine the structure of the DNA helix. The XRD pattern obtained in 1953 by Rosalind Franklin is shown in Figure V.7. Crick and Watson inferred the double helix structure of DNA from this data and were awarded the Nobel Prize for discovering the structure of the molecule of life. The spots which form a large “X” are used to calculate the pitch of the double helix. As is well known, the ladder like DNA molecule is twisted like a screw. If the twist in the DNA molecule were larger, the angle of the cross would have been smaller. The distance between the spots shows that the nucleotides which form the steps in the ladder are separated by 0.34 nm.

Another interesting example, the study of quasi crystals is also shown in Figure V.7. Theories of solid state suggest that 5 fold and

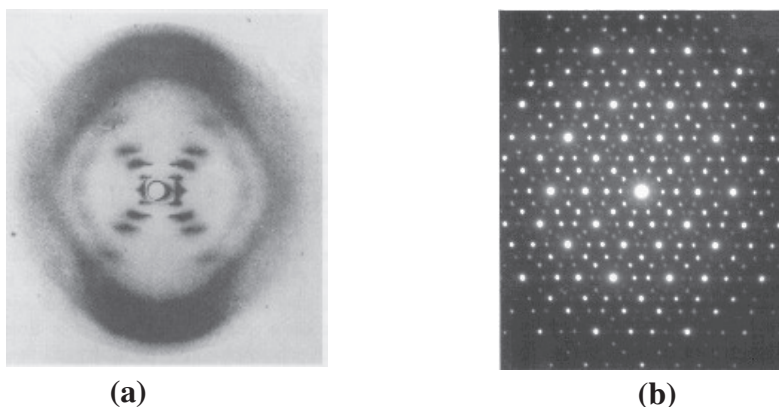


Fig. V. 7 (a) The XRD pattern of DNA obtained by Rosalind Franklin in 1953. The angle of the cross gives the pitch of the helix. The Astbury spot at 3.4\AA at the outside edge corresponds to inter nucleotide spacing, and the spots along the cross correspond to the distance between repeats of the helix (i.e. the pitch). (b) Typical diffraction diagram of a quasi-crystal, exhibiting 5-fold or 10-fold rotational symmetry

10 fold symmetry, an atom being surrounded by 5 or 10 neighbors, is not possible. Hence, materials were not expected to show this type of ordering. This is easily understood by trying to cover the floor with regular pentagons. After a few pentagons are placed sharing a side, large gaps have to be left. In contrast, it is easy to fill a plane area with equilateral triangles, squares or regular hexagons. It was argued that leaving large voids would require a large amount of energy and that such solids would not exist. In most common materials, 2, 3, 4 and 6 fold symmetries are seen. However, these prohibited symmetries were also observed in special materials which are now called quasicrystals. The spots in the pattern shown in Figure V.7 shows groups of spots forming regular pentagons and ten spots arranged regularly around a central spot confirming these symmetries.

Another very exciting example of the ability of the diffraction techniques was the determination of the electron density with an accuracy sufficient to identify the d orbitals of copper, discussed into the last chapter. Those results were obtained using the calculation procedures discussed here. In a liquid, the atomic movements are too

large to maintain any order but there is a local order which can be experimentally confirmed by diffraction methods. The modern microscopic techniques permit the direct visualization of defects such as dislocations and faults. In some cases it is also possible to consider theoretically their contribution to the diffracted intensity and confirm their presence by comparison with experimental measurement of the scattered intensity. The techniques considered so far permit a fairly accurate understanding of the positions of atoms in a solid. They permit the modeling of the order. In a very indirect way, diffraction techniques permit the identification of atoms. The amount of radiation scattered by an atom depends on the number of electrons present in the atom. Hence, the arrangement of various types of atoms can be modeled. However this is not sufficient to identify the atoms present directly and accurately. Diffraction methods also do not enable the identification of the interactions between atoms, formation of bonds, transfer of electrons and so on. For this type of information, the probe electrons or photons must exchange energy with the atoms. This is achieved during inelastic scattering of electrons and photons.

Identifying atoms and bonding

The most powerful probe for identifying the atoms present in a solid and their bonding is photo electron excitation. Using a photon of suitable energy, X-ray or UV light, electrons from the atoms are removed. The excess energy of the incoming photon is then transferred to the photoelectron as kinetic energy, which is measured accurately. Knowing the energy of the incident photon, the binding energy of the photoelectron is determined. This is the difference between the energy of the incident photon and the measured kinetic energy. The binding energy is the energy required to separate the electron from the atom and is a fundamental property of the atom. Since the binding energies of the various levels of any atom have been tabulated and are available for comparison, it becomes possible to identify the atoms present. The kinetic energy of the photoelectrons is typically less than 1000eV. Electrons emitted from less than 3nm of the sample surface can only emerge without loss of energy and be detected. Thus the method becomes a means of determining surface composition. Since the energy of a UV photon is lower, the kinetic energy is also smaller and

the information depth is correspondingly smaller than for XPS. It is necessary to perform the experiment in ultra high vacuum (UHV) where the pressure is less than 1 part in 10^{12} of the atmospheric pressure. Only this ensures that the surface is clean and that enough photoelectrons from the sample can be collected and their energies determined. Due to bonding, electrons are transferred from one atom to another, and thus the binding energies change, typically by a few eV. The atom losing an electron due to bonding has more nuclear charge and less electronic charge, so the remaining electrons move closer to the nucleus and have a higher binding energy. The reverse happens for an atom gaining an electron. Comparing different materials and standard references it is possible to obtain a very detailed picture of the various bonding states of an atom present in the sample. Figure V.8 shows a representative example of an XPS spectrum. Using modern computers, it is possible to de-convolute (separate) the complex trace into several individual peaks as shown. By comparison with standard samples, each peak can be identified as caused by a particular bond. The binding energy increases from 287 eV by 2-7 eV. This indicates shifting of electronic charge away from the carbon atom. Among the five de-convoluted peaks, C-C is the largest peak. C=O, C-O-R (R is an organic group such as CH_3) are the next two.

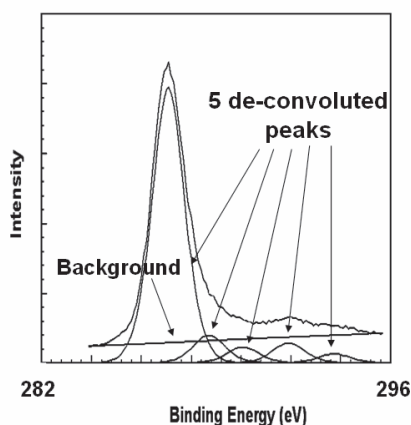


Fig. V. 8 XPS spectrum showing the various bonding states of carbon in a sample

The next peak is attributed to C-O-O-R and the final one to the double bond (δ - δ^*). By determining the area under the individual peaks, it becomes possible to determine the relative abundances of these various bonding states. A similar procedure is used to quantitatively determine the composition of the sample and the concentration of impurities.

A related technique is called the Auger electron spectroscopy (AES). The Auger process is a complex quantum mechanical phenomenon involving the interchange of energy between several electrons. As in XPS, an incident particle of high energy is required. Usually this is an electron. As in a photoelectron process, the incident energy is used to knock out an electron from the atom. If this is an inner electron, the vacancy is filled by one of the outer electrons. The excess energy available with the outer electron is transferred to a second outer electron which escapes and is detected. These electrons can be identified since their kinetic energy is related precisely to the energy of the second outer electron being ejected and the difference in energy levels between the outer and inner electrons. Thus an Auger electron is identified by three letters, KLL for example, which denote the level where the vacancy is created (K), the level from which an electron has filled the vacancy (L) and finally the level to which the emitted electron belongs (L). This process is schematically shown in Figure V.9. The depth from which Auger electrons can escape, the

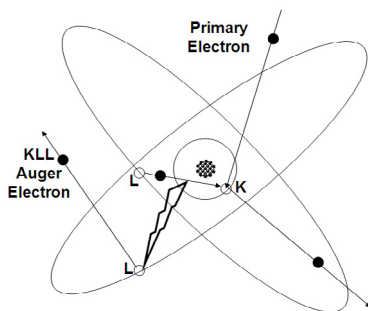


Fig. V. 9 The Auger process involving the transfer of energy between four electrons

information depth, is slightly smaller than that for photoelectron techniques. AES cannot be used to detect the electronic transfer between atoms but is a very powerful means for identifying surface atoms and determining their concentration. Since three levels are involved, understanding the electron transfer is complicated but features can be more easily seen. As in XPS, the actual measurements depend on availability of standard data.

The above techniques require the use of UHV systems. They also provide only the surface composition. It is possible to slowly remove the material layer by layer and determine the composition. This is generally achieved by bombarding the sample with ionized argon atoms accelerated to about 1000-5000 volts. Determining the thickness of the material removed is not easy and adds another complication in using these techniques for quantitative measurements.

EDAX is a much simpler technique which can be performed in an electron microscope, thereby permitting both structure and chemical identity to be determined at the same time. EDAX is energy dispersive X-ray analysis. An electron beam with much higher energies than that used for AES is used. This permits the innermost electron of an atom to be ejected. Then the outer electrons fill the vacancy and release the excess energy in the form of an X-ray photon of appropriate

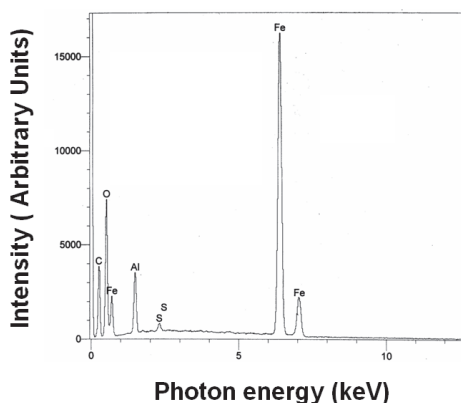


Fig. V. 10 A sample EDAX of rusted iron showing the presence of impurities. (Data courtesy Mr. K N Sood NPL)

energy. All the atoms present in the sample simultaneously emit the characteristic X-rays. These are then separated according to the energy of the X-rays and compared with standard data for determination of the composition. Since electron beam rather than high temperature is used, the sample need not be destroyed. Sample result shown in Figure V.10 demonstrates the use of EDAX for compositional analysis. The data taken from a piece of rusted iron shows the presence of impurities such as sulfur, carbon and aluminum in addition to iron and oxygen. The area under the individual peaks is determined using modern computers to provide the composition, including the various impurities present. The information depth is several microns. This depends on the wavelength of the emitted X-rays as also the energy of the electron beam. The accuracy of composition determination depends on standards used.

More than 75 years later, Sir C V Raman (see picture in Figure V.11) remains the only individual to have achieved a Nobel Prize in a science subject for work performed in any underdeveloped country. He received the Nobel Prize in Physics in 1930 for his work on light scattering in liquids and the discovery of Raman Effect. Raman Effect



Fig. V. 11 Sir Chandrasekhara Venkata Raman

is normally associated with other optical spectroscopy techniques. In view of the present classification of scattering of electrons and photons, it is included here as an inelastic scattering of photon probes with photons being detected. It is also the only process considered so far, where the energy of the emitted photon can be higher than that of the incident photon. In a typical Raman spectroscopy experiment, a photon incident on a molecule is absorbed and re-emitted. The emitted photon has an energy different from that of the incident photon. This difference in energy corresponds to the energy of vibration of one of the bonds present in the molecule. When the energy is transferred from the incoming photon to the vibration, the emitted photon has lower energy. However, it is also possible that the molecule transfers the energy available in the vibrating bond to the incoming photon and a photon of higher energy is emitted. The bond energies of the molecules are well known and Raman process can be used to identify the presence of bonds and changes in bond energies caused by sample preparation methods.

Raman lines observed for carbon nano tubes of 1.2-1.6nm diameter are shown in Figure V.12. Three lines have been identified. The peak at $225\text{-}310\text{cm}^{-1}$ (cm^{-1} is a unit obtained as $1/\text{wavelength in cm}$) is the radial breathing mode (RBM) of the vibrating nanotube. As the name suggests, the carbon nanotube diameter is increasing and decreasing just as the dimensions of the lung would increase and

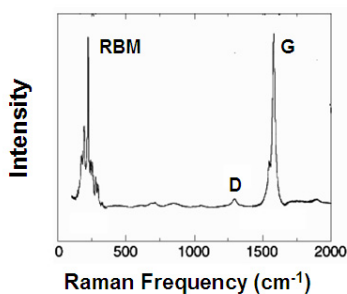
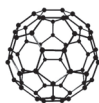


Fig. V. 12 Raman spectrum obtained from a carbon nanotube

decrease during breathing. The actual shape and position of this band would depend very critically on the diameter of the nanotube. The band is subdivided into smaller lines each of which can be attributed to a specific geometry of the vibration. For example, it would be possible to distinguish the circular shape changing into an oval and back into a circle from a vibration in which the circle is deformed into a more complex wave like shape with several nodes. It is very interesting that these deformations and vibrations occurring on a nanometer sized tube can be clearly identified using the Raman scattering technique. The weak D line at $\sim 1250\text{ cm}^{-1}$ is due to defects and deformation of the graphite hexagon. The G line at $1500\text{-}1600\text{ cm}^{-1}$ provides information regarding the electrical resistance of these nanotubes. This line position and shape are different for carbon nanotubes exhibiting semiconducting behavior and those exhibiting metallic conduction. Once again it is important to appreciate the capabilities of these techniques in providing detailed information of properties such as conduction. Determining the actual resistance of a nanotube would obviously be very difficult as it is difficult to make electrical contacts to them.

There are many other techniques for investigating the neighborhood of the atom. Some of these cannot fall into the simple classification scheme introduced here. Even the techniques that have been introduced here have been simplified for providing a basic understanding of the process whereby matter is probed. A fundamental understanding of materials is not possible without a precise understanding of the arrangement of atoms and their local interactions. The extensive development of this ability over the last hundred years has been necessary for the advances in materials development.



VI Physics of Living

Learning from nature

In the quest for new materials, systematic understanding provided by chemistry and subsequently the sophisticated techniques of characterizing the local environment of the atom in the materials have played major roles. The first materials used by man were of course naturally occurring stones, bones and sticks. There has been simultaneously an extensive effort of modifying naturally occurring plants and animals. The significant success achieved in domesticating animals and breeding plants for agriculture did not initially provide the confidence in man that the processes employed by nature could be imitated or controlled. Selective breeding of animals and plants continued to be an art rather than a science, even till the middle of the twentieth century. While the experience of animal and plant breeders was a major influence on Darwin in developing the theory of natural selection, it required the emergence of population genetics that synthesized Darwinian selection with Mendelian genetics before the processes of life were understood on a scientific basis. It required the further development of molecular biology starting with the elucidation of the structure of DNA to provide a proper scientific understanding of ways by which complex biological materials were made by living organisms. To appreciate the recent interest in genetic engineering and emulation of self organization as techniques of materials development, it is necessary to appreciate some of the latest developments in biology.

To provide a definition of “living being” is very difficult. Every definition can be questioned as being either incorrect or vague. It can

be accepted that living beings maintain an internal order of molecules while permitting the exchange of atoms and energy with the environment. In this view, creating a new generation is another means of perpetuating the internal order. The process whereby the genetic information is used to maintain the internal order of living beings is now well understood. Living organisms need energy for maintaining this order. The processes used by living organisms to acquire the required energy have also been discovered. Finally, important steps in the 3.5 billion year progress of life from the first unicellular organisms to man have also been identified. These will now be considered. The physical processes will be emphasized so that the current approaches of materials development can be appreciated.

The processes of life

The DNA (deoxyribonucleic acid) is now known to be the means of achieving and maintaining the internal order. In a living organism it is almost impossible to identify any single part as being the most important. Every part of the living system has a specific role to play in the operation of the life process. In spite of this, the DNA is rightfully designated as the molecule of life, since it contains the information vital for creation and maintenance of life. DNA is a long polymeric molecule. The human DNA stretched as a single strand is about a meter and half in length. The structure of DNA molecule is shown in Figure VI.1. This is built by repeating a basic monomer consisting of alternate molecules of a sugar and a phosphate radical. The sugar used is a five member ring called deoxy-ribose. Each of the sugar molecules is connected to a nucleotide. There are four of these nucleotides which at first sight appear to be randomly attached to the sugar. These are Adenine (A), Cytosine (C), Guanine (G) and Thymine (T). One type of order is immediately observed. Thymine and Cytosine consist of a single carbon nitrogen ring and are smaller than Adenine and Guanine which consist of two rings with a shared side. A further symmetry is that the shapes of the molecules are such that two hydrogen bonds can form between A and T and three can form between C and G. When the hydrogen bonds are formed, the length of the combinations A-T and C-G are exactly equal. Thus when two chains of DNA are placed side by side, a series of hydrogen

bonds can form; binding the two chains together provided, an A on one chain is matched to a T on the other, T with A, C with G and G with C. A closer observation of a real DNA immediately reveals that this symmetry is in fact always present. The two chains which bond together automatically become complimentary as shown in Fig VI.1.

The use of hydrogen bonds ensures that the energy required to separate the two chains is relatively small. If covalent bonds were formed, it would not be possible to selectively break these bonds while retaining the phosphate-sugar backbone intact. The complimentarity of the two chains ensures that it is possible to make two copies of the original pair very easily. Once they are separated, ACTG can be matched with TGAC. Since the individual nucleotides are available and are moving around in the cell, they will automatically get attached by hydrogen bonds to the correct location. The sugar phosphate backbone can then form, completing the copy of the DNA. This ability to make two copies of the original mirrors the ability of the living organisms to procreate; produce more of the same with identical order. Along with the hydrogen bonds acting as bridges, the

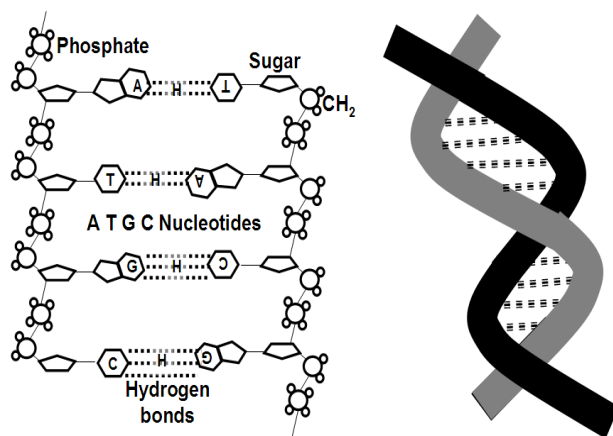


Fig. VI. 1 The DNA consists of backbones of sugar and phosphate with hydrogen bonding between the nucleotides on the two complimentary strands. The twisted helix is the final three dimensional picture.

two strands of DNA form the famous double helical structure. It looks like a twisted ladder with the hydrogen bridges between the nucleotides forming the rungs and the long chains of sugars and phosphates forming the sides of the ladder.

A closer examination of DNA shows that the nucleotides are only apparently random. The nucleotides provide the information in a digital code. The information is required to form the rest of the molecules in the living organism, which in turn are able to make copies of the DNA, to complete the circle and exhibiting the basic property of living beings: “maintaining an internal order”. Energy is required for maintaining this ordered or lower entropy state. The living organism acquires the required energy from the surrounding, by way of solar energy in the case of plant cells, and molecules of food in the case of other cells. Parts of the DNA are used to prepare molecules required for maintaining the order in the present living organism. The entire information may be copied in order to make one more copy of the living organism.

A single strand of DNA will acquire a second and will be converted into the double helix. This ability is very useful to the DNA in making copies of itself. Obviously, the DNA by itself cannot perform any action of the cell. It can only replicate. The cellular activity has to be performed by other biomolecules. These are the proteins. The DNA should have the information to produce these molecules which increases the chance of replicating the DNA and prolonging life. Proteins are polypeptides, polymers formed by joining a large number of amino acids. Proteins in all living organisms are made of 23 known amino acids. A typical protein in the cell may consist of several tens of thousands of amino acids formed according to the coded information available in the DNA. However it is necessary to have an intermediate step. It is not possible for a DNA to build a protein directly. Before the polypeptide is formed using the information available in a single strand, the DNA will become a double helix once again. The information cannot be decoded from the double helix. This intermediate function is performed by the RNA (ribonucleic acid). The change in the sugar with the hydroxyl group replacing the hydrogen and the replacement of Thymine by Uracil ensure that the

RNA does not form a double helix. The nucleotides used for DNA and RNA are listed in Table VI.1. In spite of these small changes, a one to one correspondence with the DNA is maintained. The RNA is then used for translating the DNA code into protein.

Table VI.1 Constituents of DNA and RNA

Molecule	Base	Nucleoside
DNA	Adenine(A)	Deoxyadenosine
	Guanine(G)	Deoxyguanosine
	Cytosine(C)	Deoxycytidine
	Thymine(T)	Deoxythymidine
RNA	Adenine(A)	Adenosine
	Guanine(G)	Guanosine
	Cytosine(C)	Cytidine
	Uracil(U)	Uridine

The conversion of the DNA information into a working protein is the most important aspect of life. This enables the formation of all the elaborate structure of life. Construction of the complex human brain as also the formation of the simple cell wall of the amoeba, are both performed by this process. The identification of the genetic code has been one of the greatest achievements of the human scientific endeavor. The code is a triplet code. Three nucleotides in the RNA (and obviously the DNA) correspond to a single amino acid. This provides for a lot of redundancy since 64 permutations are possible and there are only 23 amino acids to code for. A few so called “stop” signs are also included to signal the starting and ending of the relevant information on the DNA. This piece of DNA between two stop signs corresponds to a single protein and is called the gene. The universal genetic code is shown in Table VI.2. The most significant fact about the code is that with very minor changes the same code is used in all the living organisms. This, more than any other piece of information, confirms that all living things on earth have a common origin and have evolved by natural selection.

Table VI.2 The universal Genetic code

First Base in Codon		Second Base in Codon			Third Base in Codon
U		C	A	G	
U	Phenylalanine	Serine	Tyrosine	Cysteine	U
	Phenylalanine	Serine	Tyrosine	Cysteine	C
	Leucine	Serine	STOP	STOP	A
	Leucine	Serine	STOP	Tryptophane	G
C	Leucine	Proline	Histidine	Arginine	U
	Leucine	Proline	Histidine	Arginine	C
	Leucine	Proline	Glutamine	Arginine	A
	Leucine	Proline	Glutamine	Arginine	G
A	Isoleucine	Threonine	Asparagine	Serine	U
	Isoleucine	Threonine	Asparagine	Serine	C
	Isoleucine	Threonine	Lysine	Arginine	A
	Methionine	Threonine	Lysine	Arginine	G
G	Valine	Alanine	Aspartic acid	Glycine	U
	Valine	Alanine	Aspartic acid	Glycine	C
	Valine	Alanine	Glutamic acid	Glycine	A
	Valine	Alanine	Glutamic acid	Glycine	G

The next very significant fact is that the process of transcription; collecting the information available in the DNA into the RNA and translation; converting the information available in the RNA to make a protein, is unidirectional. The protein cannot influence the formation of the DNA. This is now called the central dogma of biology. However, it is more like the law of conservation of energy. Violation of these principles has not been observed. The proteins can influence which part of the DNA is used to produce a protein. This is called expression of the gene. There is however no mechanism for incorporating a change in DNA because it is required. Thus, the third most important conclusion is that changes in DNA, called mutations, are always random. This provides a molecular basis for Darwinian evolution. A mutation that promotes survival of the living organism, and thereby increases the number of its progeny, is retained. Those which are detrimental to the organism are lost due to the inability of the living

being to compete and survive. A fourth aspect of the genetic code is that the code is completely random and is not related to the structures and shapes of the amino acids or the nucleotides. To understand this, the translation process has to be observed more closely. This process is schematically illustrated in Figure VI.2. A small piece of RNA is shown. Once an RNA strand is copied from the DNA (This is called a messenger RNA or m-RNA.), it is available for translation. A molecule called a ribosome acts as a scaffold for the process and holds the m-RNA. Molecules called the t-RNA (transfer RNA) are then able to match their anti codons with the triplet code of the RNA. The anti-codon works on the same complimentarity principle as the second strand of the DNA double helix. AUG is the anti-codon for UAC since U always pairs with A, and C pairs with G. The other end of the t-RNA molecule has a space where the amino acid corresponding to the anti-codon is temporarily held. When the ribosome places two t-RNA molecules against the m-RNA, a bond, called the peptide bond, forms between the two amino acids. The first t-RNA molecule releases the amino acid and is in turn released by the ribosome permitting the addition of one more t-RNA molecule

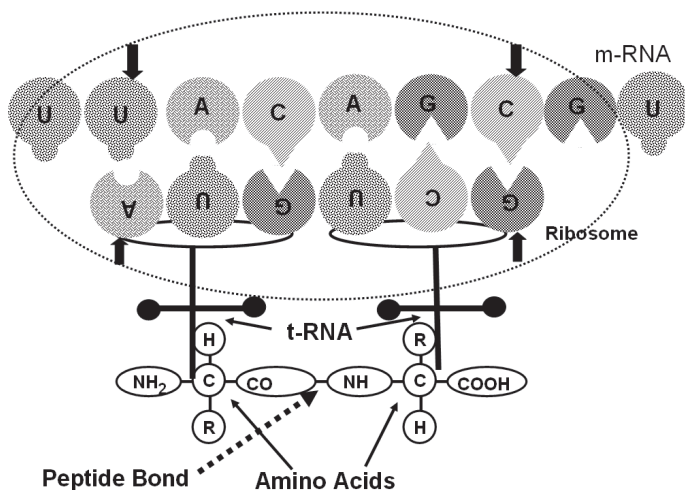


Fig. VI. 2 A schematic view of the process of translation from the m-rna to a peptide which involves the action of the ribosome and the t-rna molecules.

and another amino acid to the chain. The key aspect here is that the shape at one end of the t-RNA molecule defines the amino acid that can be fixed there. The shape of the anti-codon molecules is responsible for the codon being coupled to the anti-codon. In all living organisms, for a specific anti-codon, the same specific amino acid is found at the other end of the t-RNA molecule. The shape of the end of the t-RNA molecule where the amino is bound is not defined or dictated by the shape of the anti codon at the other end. Obviously, the particular combination observed in all living organisms is a random choice. It was first employed by primitive life forms and its use continues. Thus, the genetic code is truly random. The universality is therefore a very significant support for natural evolution.

The process of living is the ability to perpetuate the internal order, while exchanging energy and material with the surrounding. This uniform internal environment with a lower entropy or disorder of a living organism (Homeostasis) is maintained by a series of feedback control loops. Feed back control involves sensing the deviation from the desired environment and providing a response signal to reduce the deviation. This process is called a negative feedback since the response acts so as to minimize the sensed signal. Some familiar examples of feedback loops are : (1) The decrease in the size of the pupil of the eye with increased light intensity; (2) The dilation of surface blood vessels to increase heat loss from a body during a fever; (3) Increase in insulin concentration to lower blood sugar; and (4) Increase in adrenalin when danger is sensed. Each observable behavior would consist of several layers of feedback control loops. The presence of the large number of reinforcing feedback loops is responsible for the robust act of living. The mystery about living organisms is not death. The real mystery is the ability of a living organism to continue to live even with significant damage to various parts of the system. In conventional engineering, such ability is normally realized by providing an extra margin of error and redundancy. Living organisms also do this. For example, the lung capacity of a human being is perhaps ten times the minimum required for living. In addition, the feedback loops lower the risk of catastrophic failure.

In most biological feedback processes, protein catalysts or

enzymes play a vital role. The polypeptide chain is called the primary structure of a protein. This is simply a list of the names of the amino acid molecules joined by the peptide bond. Figure VI.3 shows the formation of the peptide bond between two amino acid molecules leading to the primary structure of protein. The bond forms between the amine and acid parts with the release of a molecule of water. The various amino acids differ only in the nature of the side chain. The sequence of the amino acids is defined by the DNA. The long chain of amino acids is folded to form helices or sheets. The folded structure is stable because of hydrogen bonding and electrostatic attraction. Figure VI.4 shows two important means of bonding between the amino acids on a peptide chain. These are the hydrogen bonds between the NH and CO parts of the chain and a sulfur bridge that forms between two cysteine molecules. While the specific regions which form bonds are identified, it has not been possible to specify the folded or secondary structure on the basis of the knowledge of the primary structure. Two primary forms of the secondary structure are the alpha helix, which twists in the clockwise direction and the beta confirmation which resembles a sheet. A further organization of the

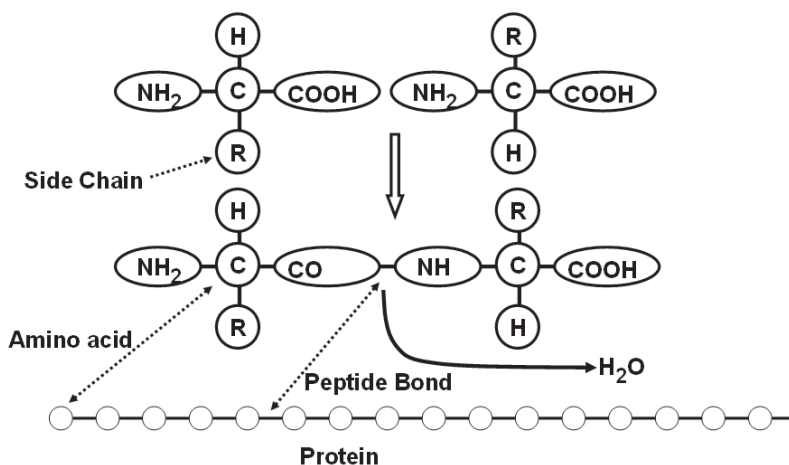


Fig. VI. 3 The formation of a peptide bond between two molecules of amino acids involves the removal of a molecule of water

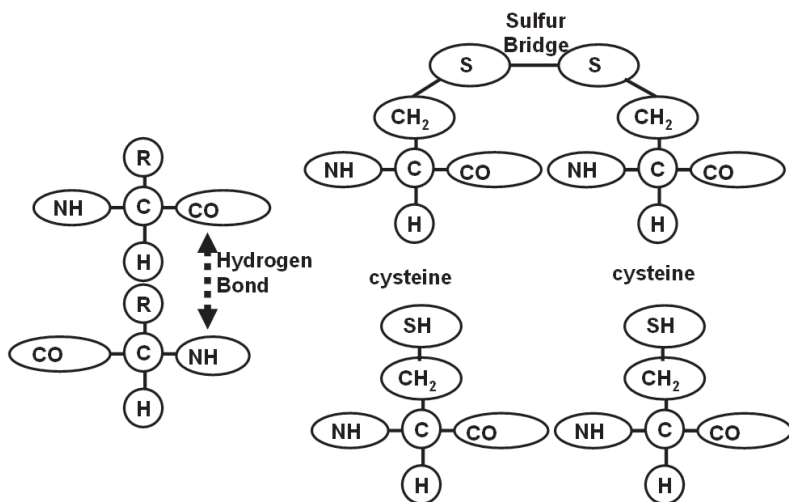


Fig. VI. 4 Folding of polypeptide is caused by (a) Formation of hydrogen bonds between the amine and acid groups and (b) formation of sulfide bridge between two cysteine molecules.

proteins results in a tertiary structure which gives the protein the functional capabilities. Most enzymes have an active site where the reactant molecules are initially adsorbed. As seen in Figure VI.5, the active site is caused by the side chains which have strong hydrophilic or hydrophobic properties. These are predominantly present at the active site and attract or repel the adsorbed molecules. The catalytic action of an enzyme is no different from that of any inorganic catalysts. By bringing the reactant species close enough, the reaction is facilitated. The use of long chains of polypeptides is a major advantage. Small changes in the polypeptide chain may sometimes cause qualitative, rather than catastrophic changes, to the enzyme function. Figure VI.6 on colour plate xv (Page 98/99) shows the complex structures of well known enzymes, insulin and pepsin.

Acquiring energy

After this brief overview of the process of living, it is relevant to look closely at the means by which living organisms acquire the energy

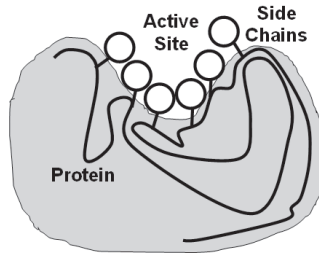


Fig. VI. 5 The active site in an enzyme is caused by the side chains of the amino acids.

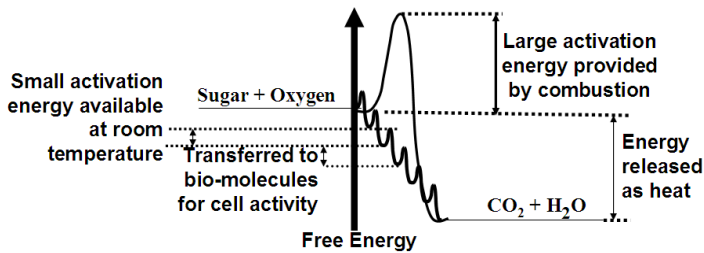


Fig. VI. 7 Thermodynamics of the combustion of sugar in fire and in a living cell.

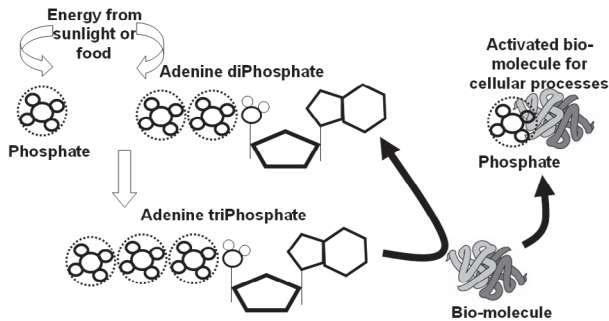


Fig. VI. 8 The universal phosphorylation approach used by cells for creating active molecules such as ATP.

from the environment in order to maintain their internal order. Not very surprisingly, the processes employed are almost identical for all living beings. This is in fact somewhat similar to the universality of the genetic code. The most general statement is that the living organisms consume food for energy. A more technical statement would be that *sugar is oxidized to carbondioxide and water and that the combustion energy is used for cell processes*. This is too abbreviated for being understood. The molecule of sugar has more energy than the molecules of carbondioxide and water which are produced by its combustion. However, sugar does not burn readily. It has to be heated in a fire before the sugar molecule decomposes. This is obviously not possible in a living organism. Further, in the process the energy is released as heat, a form which is not useful for a living organism. A living being is not a steam engine. In a living being the sugar molecule is converted to the final combustion products in a series of steps. At each step, the input energy required to initiate the reaction is small enough to be available at the normal living temperature. If necessary, such reactions can be further catalyzed by enzymes. This is illustrated in Figure VI.7. At each step of the reaction a number of activated carrier molecules are the reaction products. Thus, the free energy released at each step is not very large and most of this is stored in active biological molecules.

In all living organisms the addition of a phosphate radical is used as the means of increasing the energy of a molecule. A phosphate radical is added to a biological molecule using the energy from the oxidation of glucose. This bio-molecule with a larger number of phosphate groups becomes the reactant for the cellular process. When the cellular process is complete, it loses the extra phosphate reverting to a lower energy state. But the purpose has been achieved. The higher energy of the reactants ensures that the reaction proceeds to completion at the normal body temperature. This is shown in Figure VI.8. The molecule most often employed for this purpose is Adenine-tri-phosphate or ATP which is dubbed the “energy currency” of the cell. The conversion of ADP (di-phosphate) to ATP (tri-phosphate) is the cell’s process of acquiring energy and the reverse is employed for cellular processes. The intermediate thermodynamic energy (neither

too small nor too large) makes ATP an ideal molecule for adding the phosphate group using external energy and removing it to facilitate cellular reactions. ATP also provides the energy for active ion transport, muscle contraction and movement of nerve impulses. All cellular processes therefore involve the addition of a phosphate radical to the reactants. Even in the case of the plants, the sunlight is not directly used for the production of carbohydrates. Sunlight is used for making ATP. Then the ATP is used for producing the sugars.

The processes by which ATP is produced in the cells are very complex. There are three ways by which ATP is produced. Each in turn is an extremely complex bio-chemical process with a large number of intermediate steps. These complex cyclic processes in living organisms are summarized in Figure VI.9. The first of these is Glycolysis. This involves a series of ten reactions by which the cell consumes a molecule of glucose and generates two molecules of ATP from ADP. This is energetically not a very efficient process. However this is observed in all living cells including the prokaryotic cells indicating that this is the oldest mechanism of sustaining life. In anaerobic bacteria such as yeast, the glucose is converted into ethyl alcohol. The fuel value of this molecule is a clear indication of the low efficiency of utilizing the energy in the glucose molecule. In muscle cells, Glycolysis results in the formation of lactic acid. In muscle cells, Glycolysis results in the formation of lactic acid. The

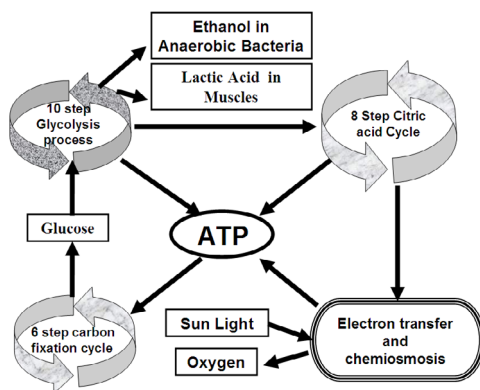


Fig. VI. 9 The different cellular processes mediated through ATP.

accumulation of lactic acid results in fatigue. In eukaryotic cells, the product of Glycolysis is a molecule of pyruvate which is further processed in the mitochondria to produce two more molecules of ATP. This complex process of eight steps is called the citric acid cycle. In addition to the two molecules of ATP, this process results in the creation of excess of protons (ionized hydrogen atoms) on one side of the mitochondrial membrane. This excess is called a concentration gradient of protons. The excess protons flow through the molecule called the ATP synthase or ATPase. In this process of chemical osmosis, sixteen more ATP molecules are generated by using the excess energy available in the proton concentration gradient. Interestingly, the first step of photosynthesis also involves similar creation of a proton gradient and formation of ATP. This process takes place in the chloroplasts where the molecules involved in electron transfer and creation of the proton gradient are similar to those found in the mitochondria. In this first step of photosynthesis, oxygen is released from the water molecule and not from carbon-dioxide as is commonly assumed. Chemical osmosis forms the first step in photosynthesis. The energy stored in the ATP is then converted into glucose for storage and used by other cells in a six step carbon fixation cycle where carbon-dioxide is consumed. The entire scheme can be observed in plants except for the production of ethanol and lactic acid. In animal cells the carbon fixation cycle and formation of chemical gradients due to sunlight are not observed. Simple bacteria employ only glycolysis. It is exciting to note that the movement, from simple to complex life forms is mirrored by these molecular processes also.

Chemical osmosis, whereby proton gradient causes the formation of ATP with a very high efficiency, is very important for all higher organisms. The mechanisms can be found in cyanobacteria which developed photosynthesis 3.5 billion years ago and served as the precursor for modern plants. In all modern multi-cellular organisms, this membrane based apparatus is found in the chloroplasts of plant cells and mitochondria which are present in all eukaryotic cells. This high efficiency process of creating ATP is essential for the emergence of complex life forms. The ATP synthase or ATPase which performs

this action can be considered as the second most important biological molecule next to the DNA. This molecule uses the energy stored in the proton gradient for converting ADP to ATP. The molecule also acts as an active molecular pump and creates an ion concentration gradient. In this process it operates in reverse and ATP is converted to ADP. The energy is used to create the concentration gradient of the ions. This reverse process is used for muscle contraction, movement of nerve impulses and so on. The elucidation of the action of this molecule in cellular processes was a major achievement and the scientists Boyer and Walker (see pictures in Figures VI.10 and VI.11) were awarded the Nobel Prize for chemistry for this work in the year 1997.

The operating principle of the molecular pump and generators is very interesting. The schematic view of this molecule is shown in Figure VI.12. The molecule shaped like an orange has a channel at the center. This channel permits the passage of protons or other ions, for example K^+ . The six parts of the orange shaped structure can alter their secondary structure. There are three stable configurations. In one, adsorbed ATP is replaced by ADP. In the second, a phosphate radical is co-adsorbed near the ADP. In the third, the phosphate radical is attached to the ADP to form ATP. The three configurations are



Fig. VI. 10 Paul D. Boyer



Fig. VI. 11 John E. Walker

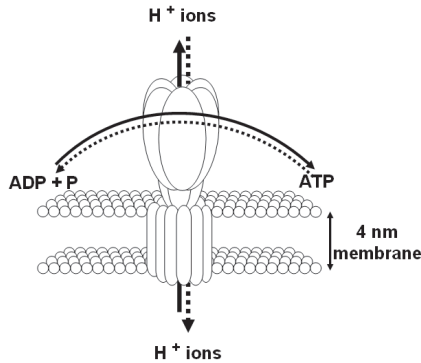


Fig. VI. 12 The ATPase molecule used to exchange energy between the concentration gradient of ions and the ATP molecule.

shown in Figure VI.13. These changes in the sub units proceed with time as the protons flow through the central channel. The timing for the different sets of subunits is sequential. This creates the illusion of the whole molecule rotating. While the molecule is not rotating, each configuration is passed on to the neighboring subunit. The direction of propagation of the configuration is reversed when the unit is used as a pump rather than as a generator of ATP. The action of the single molecular motor discussed earlier can now be understood properly.

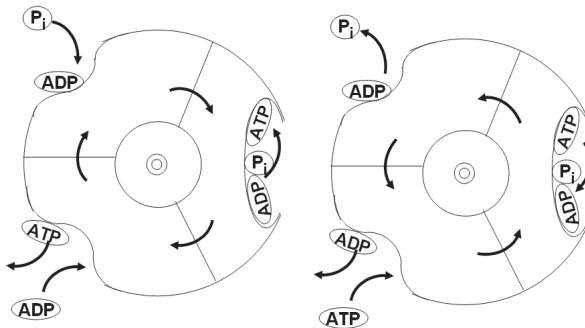


Fig. VI. 13 The changing configurations of ATPase Molecule driving the process of exchange of energy between the chemical gradient and the ATP molecule.

The ATPase molecules are present on the mitochondrial or thylakoid (chloroplast) membranes which are otherwise impervious to protons. Thus the concentration gradients can be increased or decreased only due to the flow of the ions through these molecules. The electron transfer systems are present on the membrane and generate the proton gradient. Extremely similar membrane bound proteins transfer electrons and create a proton excess on the outside of the thylakoid membrane due to oxidation of chlorophyll by light, and on the outside of the mitochondrial inner membrane due to oxidation of glucose in the citric acid cycle. The similarity is shown in Figure VI.14. Both are two step processes. The detailed molecular structures of these complex molecules which are attached to the membrane and create the concentration gradient in photosynthesis and citric acid cycle are quite similar. The similarity is once again an example of the natural selection employing existing structures for novel uses. While the process of generating the ATP molecules is quite efficient in comparison to Glycolysis, the absolute efficiency of plant photosynthesis is quite low. The energy stored in ATP is theoretically less than 20% of the energy of the incoming photon even when the lowest photon energy is assumed. In terms of energy radiant on unit area, the typical efficiency of photosynthesis is only ~1%.

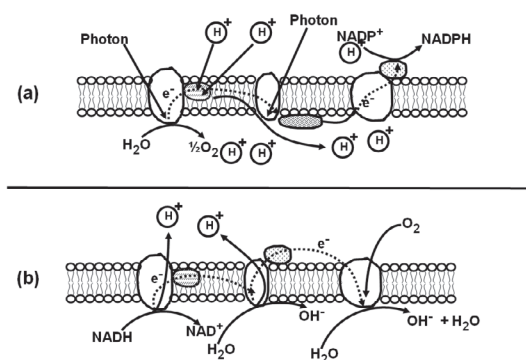


Fig. VI. 14 The electron transfer in chloroplasts and mitochondria resulting in gradients of proton concentration.

Progress of life

Life has emerged on planet earth at least 3.5 billion years ago. This is confirmed by fossilized remains. One of the oldest fossils of living organisms is shown in Figure VI.15 on colour plate xvi (Page 98/99). The rock is 3.5 billion years old. The biological origin of the microscopic remains has been confirmed by Raman Spectroscopy. According to current knowledge, this is less than a billion years after the formation of the solar system. Efforts to consider the emergence of life as an extra terrestrial phenomenon would not answer the question of how life has emerged from the inanimate matter. The extra terrestrial claims only offer a vague statement that life has not originated on earth.

The experiments by Urey and Miller demonstrated that the basic building blocks such as amino acids could have formed by the action of electrical discharges and ultraviolet radiation on the reducing atmosphere. It is known that such an environment was present on the earth during the early years after the formation of the solar system. This is a good model for the formation of complex biological molecules. With the understanding provided by molecular genetics, Darwinian evolution of all the life forms on the earth from a common unicellular organism has been extremely well confirmed. However, the complexity of even the simplest bacterium is truly astounding. The cell is an individual living organism which performs thousands of complex processes in order to stay alive. The link between the simple biological molecules and the complexity involved in the simplest of living cells has not been so far bridged by science.

Three most important steps can be identified in the history of the Darwinian evolution of life on Planet earth. The first is the emergence of cyanobacteria which have altered the basic environment of earth. The second is endosymbiosys which has resulted in the formation of the eukaryotic cells, the precursor for all complex life forms. The third and final step is the emergence of the modern man, who has developed the ability to understand and control the process of biological evolution.

One of the early living organisms, Cyanobacteria, developed

photosynthesis, the ability to use solar energy for acquiring the energy for life processes. There is evidence to suggest that prior to this, cells were acquiring energy from other high energy molecules such as H_2S . Such primitive organisms are still present on the earth. Cyanobacteria achieve high efficiency of energy acquisition by using the chemical osmosis process discussed earlier. They started releasing free oxygen. This ultimately led to the formation of an oxidizing atmosphere. The free oxygen generated initially by cyanobacteria and subsequently by plants has been responsible for the formation of iron ore, sometimes called banded iron, due to precipitation of iron which was then present in the form of soluble iron salts in the sea. Once the iron present as soluble salts was exhausted, the oxygen was consumed and red beds formed on land due to oxidation. Figure VI.16 shows a quantitative estimate of the consumption of free oxygen produced by life processes. Only a small fraction (4%) exists in atmosphere as molecular oxygen. The accumulation started around 2 billion years ago and the present concentrations were reached less than 0.4 billion years ago. The change in the oxygen concentration estimated from various scientific

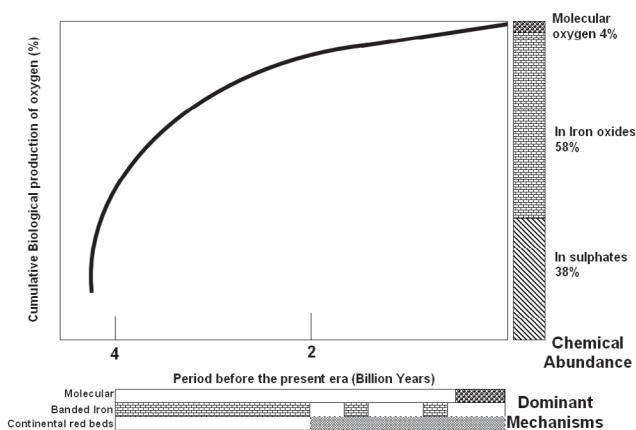


Fig. VI. 16 A quantitative estimate of the production and subsequent use of free oxygen released in earth's atmosphere by the process of life.

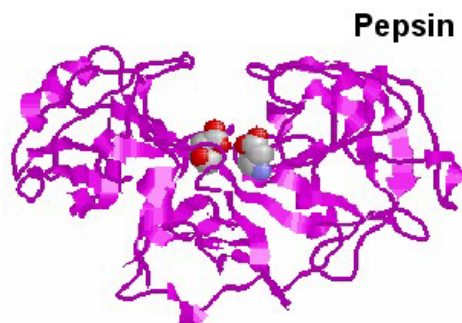


Fig. VI. 6 The complex structures of common enzymes, insulin and pepsin. The ribbons are amino acids bonded together as helical and sheet (secondary) structures.

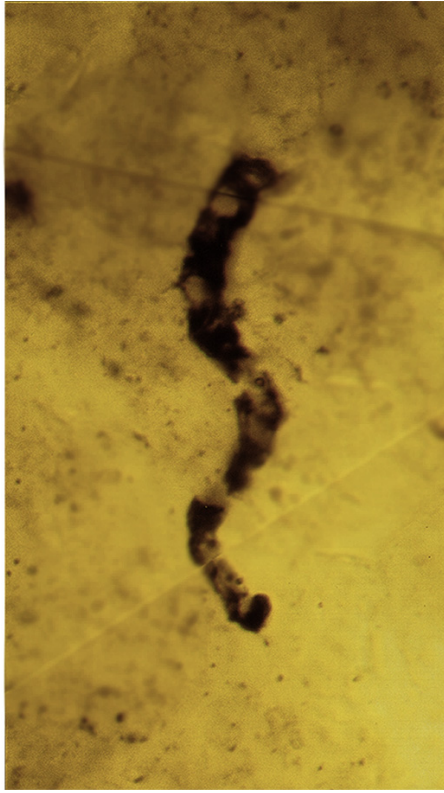


Fig. VI. 15 An image of the oldest fossil formed ~3,465-million-year-old Apex chert of Western Australia. (Used with permission of Prof. J. William Schopf).

studies is shown in the Table VI.3. It is interesting that not merely the fossil fuels, petroleum and coal but even the iron ore responsible for industrial revolution, is a byproduct of biological processes. It is significant that the free oxygen availability could not even start till alternate processes that could consume oxygen were completely saturated. While the influence of human beings is merely to increase the concentration of carbon dioxide by a few hundred ppm, life has converted the initial reducing environment on earth to the present one having high free oxygen content. The increase in free oxygen concentration to significantly higher levels 350 million years ago was responsible for the accelerated growth of trees. These ancient forests are the source of the coal used presently.

Table VI.3. Estimated variation of oxygen concentration

Estimated Concentration of atmospheric oxygen (%)	Time before present (Billion years)	Important Biological events
< 0.5	> 3.5	Ozone layer
0.5	~3.5	Cyanobacteria
1	~2.0	Eukaryotes
10	~1.0	
20	0.4	Large animals
35	0.35	Tree growth
15	0.29	Extinctions
20	0	Civilization

The next major step in the history of life is the emergence of Eukaryotes. These are cells where the genetic information, the DNA, is contained in a separate nucleus. Thus when the cell divides, a copy of the DNA has to be made. This is called cell mitosis. In true bacteria which do not have a nucleus, the DNA double helix is in the form of a ring. Multiple copies are already available in the cell and a new cell can be formed by simple division since copies of the DNA will be already present in the two parts. The schematic view of the animal and plant cells in Figure VI.17 shows the nuclei of the cells which contain the familiar chromosomal DNA. Ring type DNA of mitochondria and chloroplasts is also shown. There are also strong

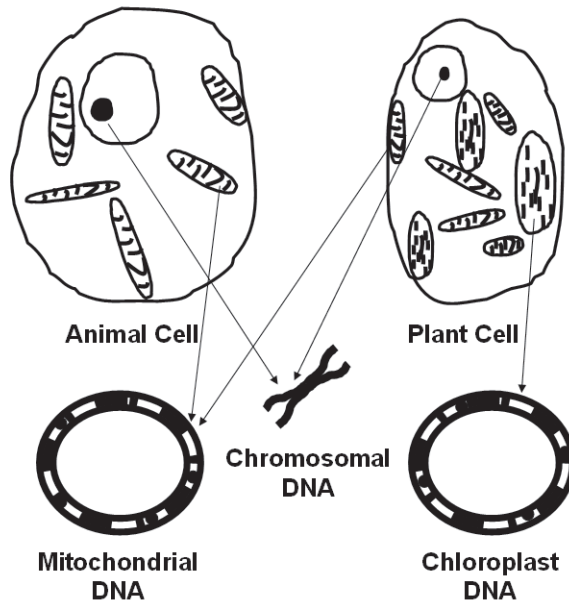


Fig. VI. 17. The DNA evidence for endosymbiosis. The mitochondria and chloroplasts retain the prokaryotic ring shape DNA in addition to the nuclear DNA of a Eukaryotic cell.

similarities in the internal structures of these two rings. It is now generally accepted that the evolution of eukaryotes, which was a very important precursor for the emergence of complex life forms, involved symbiosis of aerobic and anaerobic bacteria. A prokaryote ingested aerobic bacteria which thus gained protection. The aerobic bacteria with a more efficient ATP production capabilities provided energy to the prokaryote. Over time, the aerobic bacteria lost the capability for independent existence and became mitochondria which are present in all eukaryotic cells. A further ingestion of cyanobacteria then led to the availability of pigments capable of harvesting energy from sun light. These cyanobacteria in turn lost the capability of independent existence and became the chloroplasts which are present in plant cells. Mitochondria and Chloroplasts have independent DNA rings distinct from the chromosomal DNA of eukaryotes and similar to the DNA

of other prokaryotes. They also exhibit cell fission rather than mitosis. New copies of these parts of the cell are formed by division. Some of the proteins required by them are made by the rest of the cell and some by the mitochondria or chloroplasts themselves. This suggests gradual changes in their original independent existence. The mitochondria are inherited generally from the mother since the sperm cell is too small and has insufficient space to provide its own mitochondria. The egg, in contrast, is a large cell that provides all the mitochondria. This inheritance and the separate DNA of mitochondria are important in understanding the history of man.

The emergence of the modern human species is obviously the latest and most important step in the history of life. Humans with the ability to understand and communicate the story of life have gained the power to alter Darwinian evolution based on natural selection. This is called artificial selection. A small beginning was made with plant and animal breeding. The recent understanding of the molecular basis of life processes has given more power. It is now possible not only to emulate the processes of life but also to control our own destiny. Fossil evidence suggests the emergence of a proto-human species, walking on two legs separated from an ancestor shared with the Chimpanzee around 5 million years ago. *Homo-erectus* emerged in Africa around 2 million years ago and his remains have been detected as far as Java and Beijing. This species is associated with both stone tools and use of fire. This is probably the first instance of a living organism being able to survive in all types of environments. Almost as soon as the person emerged in Africa he has been able to live not only in the grasslands of Africa but the temperate zone of China and the equatorial jungles of Indonesia. It was long expected that modern human beings evolved in various parts of the globe over the last 2 million years ever since human remains were found as far apart as Africa, China and Java. Molecular genetic study of the present human population, however, has provided robust evidence that the modern man has existed as a small band in Africa about 100,000 years ago and has begun the colonization of the rest of the world less than 70,000 years ago.

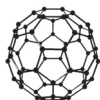
Mutations are small changes that always occur when the DNA is

copied from one generation to another. The rate at which such errors occur can be experimentally determined. This is different for the mitochondrial DNA and for the chromosomal DNA in the nucleus. In humans, mitochondrial DNA is inherited from the mother to the daughter alone. Similarly the Y chromosome is inherited only by the sons from the fathers. Modern experimental techniques have enabled unraveling of the entire human DNA (the human genome). It is then possible to use high power computers to identify the copying errors that have been incorporated. The combination of the rate of errors and their location can then be used to identify the common ancestor of any two living organisms. The process becomes extremely accurate in constructing the human family trees. Figure VI.18 shows the exciting results obtained. It is now clear that three small tribes with a common ancestor emerged in Africa about 100,000 years ago. Three maternal lineages based on mitochondrial DNA and three paternal lineages based on Y chromosome evidence have been identified. One tribe has expanded into Asia 56,000-73,000 years ago, into Europe 39,000-51,000 years ago and America 8,000-35,000 years ago. The formation of new tribes eventually leading to 18 female and 10 male lineages have been identified. These results show that of race, ethnicity and inherited superiority are wrong. The impact of these scientific results on social sciences can be expected to emerge in the future.



Fig. VI. 18 The current picture of migration of man from Africa. There is more genetic diversity among Africans since the rest of all the humans originated from one of the three lineages from E and A..

Living systems are extremely complex. A mature understanding of chemistry was required before the analysis of biologically active molecules could even begin. The synthesis of urea showed that organic molecules obey the same principles of chemistry as the others. It required a further hundred years of development before Pasteur could come up with the germ theory of disease. The sophisticated experimental techniques had to be refined before they could be used to determine the molecular structure of living molecules. This knowledge is now being used for developing the latest approaches of materials development. Several examples of modern materials such as biosteel developed using genetic engineering, nanometer sized motors using ATPase and self organization of nanomaterials have been introduced earlier. The recent advances in our understanding of processes of life are critically important for these technological developments.



VII Experimental Method and Principles of Physics

Concepts of chemistry, techniques of probing matter and a physical understanding of living systems have all successively contributed to the development of newer materials. Materials development has to be experimental. The material properties must be experimentally verified. The new techniques of materials development have to be experimentally confirmed. This, however, is a very simplistic view of the experimental approach. The principles of physics have a very much deeper linkage to the experimental method. This is not very much emphasized in conventional textbooks of physics and is discussed here to explain the power of the experimental method. The counter-intuitive results of quantum mechanics, such as tunneling and wave particle duality, have been seen to be quite real and necessary for exploring and developing materials. These have been briefly introduced at various points during the discussions so far. An electron behaves like a wave in the electron microscope and like a particle in Auger electron spectroscopy. Tunneling is needed to account for the scanning tunneling microscope and for understanding the principle of radio isotope dating. Quantum uncertainty is an important limitation to be considered for the femtochemistry experiments and an important basis for understanding the nature of inter atomic bonding. A necessarily brief but hopefully useful introduction of these two issues, nature of experimental science and quantum reality is presented here.

Understanding the experimental approach

It is possible to outline some very basic requirements for using an experiment as the basis for generating an understanding. Nothing is

being assumed, except a simple statement that the experiment shall be the basis for generating the knowledge. The first requirement will then be that the experiment should have preferably one most probable result or a small number of possible outcomes. It is not meaningful to say that a lottery is an experiment. The only prediction that can be made is that one of the contestants of the lottery would be successful. Of course, one can evaluate the lottery for possible biases to see if all the contestants have the same chance of winning. This would be a meaningful experiment since there are specific possible results; the reality of the bias and the magnitude of the bias if any. In general, a useful experiment has a few possible outcomes. The whole of science rests on the ability to select one of the outcomes, on the basis of a theory and then conclude that if the experiment does not confirm the prediction, the theory is to be rejected or modified.

A second requirement for an experiment is that the total probability of the various possibilities is unity. This is not to say that all the outcomes of the experiment are known. In any real experiment there are always possibilities which cannot be known in advance. However, these surprising results usually have a very low probability. The sum of all probabilities being unity is a very useful premise in selecting a theory. The experiment must give one of the several possible outcomes. This is the practical consequence of the demand for the total probability being unity.

Further, an experiment that cannot be repeated is useless. Thus it is necessary that the experiment be repeatable anywhere. Shifting the experiment to a new location or changing the orientation should not change the outcome. Similarly, the experiment must be repeatable anytime in the future. The constraints that the experiment be repeatable at any place and at any time are apparently quite simple. However, sometimes it can be observed that the experiment is repeatable only for a limited change in the location or time. For example, a simple pendulum will give the predictable performance when it is moved about on the earth but not when it is shifted to a spacecraft. Even on the earth, moving the pendulum to the top of Mount Everest or to the South Pole can change the results significantly. However, by observing the operation systematically, it is possible to confirm that the

experimental setup is not isolated and that there are physical signals being received from outside the setup, which are influencing the results.

The influences from outside the experimental setup have to be small if the results of the experiment are not to change due to shifting the setup. In case there are influences from beyond the local region, it should be reasonable to expect that there is a physical mechanism responsible for influencing the experiment. In the case of the simple pendulum the non-local influence is the earth's gravity. Since this is a physical phenomenon, it is possible to understand the changes in the experimental results. If the non-local influence is important, non-local changes will be physically transmitted to the experimental setup. As a thought experiment, if the earth's gravity suddenly changes by a large amount, the changes should be physically transmitted to the experimental setup. Obviously if such a transfer is physical, it must have a finite velocity. To summarize, an experimental result should have: (1) A small number of possible outcomes with a total probability of unity; (2) Constancy of the experimental results when repeated at a different location in space and time; and (3) A finite velocity with which non-local changes influence the experiment.

Principles of conservation

All this appears to be an elaborate description of the obvious. It may sound like a discourse in philosophy. However, it turns out that the experimental constraints; of being repeatable at different places, at different times and when oriented in different directions, lead to the principles of conservation of linear momentum, angular momentum and energy. To mathematically prove this is easy, in the case of Newtonian mechanics. However, rather than the classical Newtonian equation, (force is the product of mass and acceleration) the action principle is to be used. While Newton's law is observed to be obeyed, it was not clear why a particle chooses a path along which Newton's law is always obeyed. The action principle was historically developed as an explanation.

This seeks to predict the path of an object as it travels from a location x_1 at time t_1 to a location x_2 at time t_2 . "Action" is defined as

the integral of the difference between the kinetic and potential energy. [Action = $\int dt(KE-PE)$] +''dt (KE-PE) The integration is performed along any imaginary path. It is assumed that the kinetic and potential energies at every point on the path are known. The action principle states that the path of stationary action is the path followed by the object. This is also the path along which Newton's law is obeyed. This equivalence can be shown mathematically. The principle of least action provided a basis for the object selecting a path along which Newton's law is obeyed.

More importantly for the current purpose, if the positions of all the particles are changed by a fixed amount, in other words, if the experimental set up is moved to a new location, the principle of least action requires that the momentum be conserved. The law of conservation of momentum is thus the consequence of the demand that the experiment performed at a different location show the same result. Similarly, the law of conservation of energy is the result of the demand that the experiment be repeatable after any delay in time. The rotation of the system by a constant angle results in the law of conservation of angular momentum. These derivations are extremely simple to prove mathematically from the principle of least action.

The point that is being highlighted here is that the common sense requirement that an experiment be repeatable, after some time or in a different location and if the orientation of the experimental setup is changed, directly leads to the laws of conservation of energy, momentum and angular momentum. Since position angle and time can be continuously changed, these are called continuous symmetries. Emma Noether is a famous mathematician (see picture in Figure VII.1) who proved a mathematical theorem which states that, associated with every continuous symmetry is a conserved entity. This



Fig. VII. 1 Emma Noether

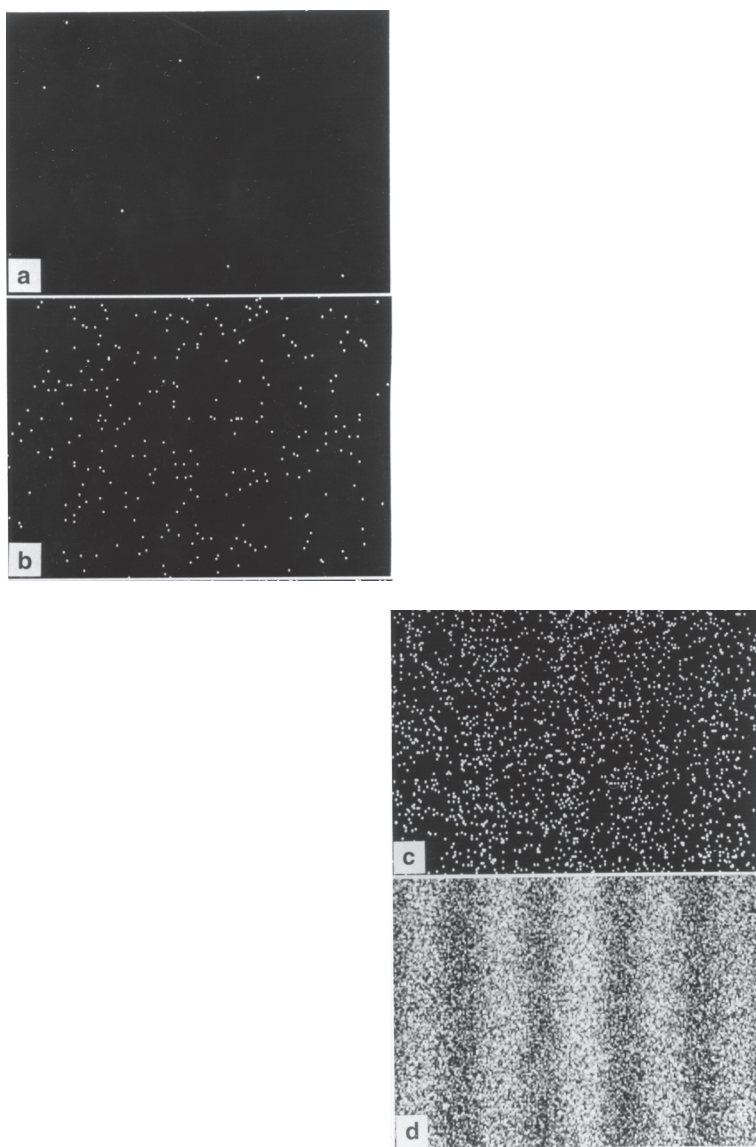


Fig. VII.2 The result of the single electron interference experiment. The individual electrons appear to fall at random locations on the screen but have a probability of reaching those areas where there is a high probability for the formation of a diffraction maximum. (Used with permission from Dr. Akira Tonomura).

is now called Noether's theorem. This generalizes and relates principles of conservation to the symmetry expected in theories of physics.

Necessity for quantum approaches

At this point it is necessary to consider the quantum nature of electrons and photons. The single electron interference experiment is the best illustration. In a typical electron microscope, electrons are produced by heating a filament. For the present experiment, the heating is reduced so that electrons are emitted one by one. This is confirmed by the individual dots that form on the screen of the electron microscope. Now a fine wire comparable in diameter to the de Broglie wavelength of electrons is placed in between the source and the screen. As seen in the screen (a) in Figure VII.2, individual dots appear. To begin with, these appear to be randomly located. The experiment is continued for a long duration. The density of dots increases as in (b) and (c). In (c), a careful examination would indicate that some vertical bands are probably forming. In (d), the individual dots merge into an interference pattern. This experiment can be in principle repeated with photons. It is impossible to visualize or describe what is happening here. Visualizing the electron as a particle explains the individual dots. The electron is moving at random and falling at a different location of the screen. But the interference pattern that emerges collectively cannot be understood at all. Imagining an electron or a photon as a wave explains the interference pattern formed in screen (d). If the number of electrons is increased, a stable pattern corresponding to the interference pattern is observed. The components of the electron wave, coming from either side of the wire, placed in front of the filament, are interfering. This is similar to the interference of waves on water surface that can be observed by throwing two stones into it simultaneously. Even the mathematics is identical. But this picture cannot account for the individual dots observed at random locations when intensity is lowered. Thus, one sees the essential quantum nature of an electron or a photon; they are neither waves nor particles. Physicists have a mathematical way of predicting the observations. The electron or photon has a probability of being detected at any point on the screen. The probability is a maximum at

the places where the intensity of the wave would be a maximum. Since the probability is maximum at these places, after a large number of electrons have been detected, (at high intensities) the interference fringes are observed. The quantum theory refuses to answer any question as to how the electron is moving from the source to the screen. In fact the theory states that any attempt at such a description would not succeed in explaining the results.

Equally clearly it is not possible to identify any single path as the path of least action. This is the reason it is not possible to consider the quantum object as a particle. The classical action principle is then altered by assuming that a quantum system evolves along all possible trajectories (paths). Each trajectory or path $\{x(t)\}$ has an “Amplitude” given by

$$e^{i \text{Action} \{x(t)\}/\hbar}$$

The “Action” for the path $x(t)$ in the quantum case is analogous to classical mechanics: the integral of the difference between kinetic and potential energies along the path. The classical statement that the particle follows the path of least action is however not accepted. The total amplitude is calculated by summing (or integrating) over all possible trajectories. The probability of observing the final result is the (absolute) square of the total amplitude. This is called the “Path Integral” approach to quantum mechanics and expresses the essential counter intuitive nature of a quantum particle. The path integral gives an amplitude which is a complex number \emptyset . The experimentally observable probability is the product of the amplitude with its complex conjugate \emptyset^* namely $\emptyset^*\emptyset$.

The probabilistic approach leads to quantization of physical quantities such as energy and angular momentum. There will be specific values for which the probability will be non zero and other values for which the probability will be zero. The quantum object cannot exist with these values of the physical parameters. For example, consider a hydrogen atom. There is a probability for the electron to have an energy of -13.6 eV. There is a region of space around the proton (which constitutes the hydrogen nucleus) where the probability of existence of an electron of this energy is non zero. Similarly the

electron can also have an energy of -3.4 eV. There is another region of space where an electron of this energy has a finite non-zero value of probability. For energy values between these two however, there is no region of space where the electron can have a non-zero probability. Thus these intermediate energy values are considered as not permitted or forbidden. This is the reason for the observation of the spectral lines which was mentioned at several places. This is the reason why the binding energies in XPS investigations can be tabulated. They are properties of an atom. However, small changes can occur as will be discussed presently. The forbidden energy and angular momentum values are a basic character of the quantum theory. This is normally stated in reverse. The permitted energy states are quantized. The permitted values are multiples of a basic unit of energy or momentum in simple systems such as a harmonic oscillator. However, sometimes not all multiples of the basic unit are observed. These absences obey rules called “selection rules”.

The probabilistic nature of quantum mechanics leads to the observed tunneling behavior in a scanning tunneling microscope. The electron has a probability to escape from the tip to the substrate. This depends on the voltage applied to accelerate the electrons, and the gap across which electrons have to escape. The current that is observed is the product of this probability and the number of electrons available. Thus, not all the electrons available escape by tunneling. Radioactivity is a similar probabilistic phenomenon. In a nucleus, there is a finite probability for a neutron to convert into a proton and release an electron. The probability depends on the number of protons and neutrons present. In carbon, it is larger for a combination of 6 protons and 7 neutrons ($^{13}\text{C}_6$) than for a combination of 6 protons and 6 neutrons ($^{12}\text{C}_6$). $^{13}\text{C}_6$ is radio active and decays to $^{13}\text{N}_7$. The number of $^{13}\text{C}_6$ which decay in a given time is proportional to the number of these atoms actually present. Knowing that the ratio of $^{12}\text{C}_6/^{13}\text{C}_6$ at the time a living object was formed is the same as in nature, and the ratio observed now, it is possible to estimate the age of the object. This is the principle of radio carbon dating. Similar techniques using isotopes of other elements are used for determining the age of rocks. These principles of estimating the age of stone tools and dead

organisms are based on the statistical nature of quantum measurements. When the radioactive decay involves the emission of an α particle (nucleus of He consisting of 2 neutrons and 2 protons), the α particle actually tunnels out of the nucleus. The similarity to the probabilistic nature of electron tunneling is obvious.

The second feature of the quantum objects is the uncertainty. Electrons and photons are neither particles nor waves. They may approximately resemble either particles or waves in certain circumstances. In an electron microscope the electron can be considered as a wave for all practical purposes. In making an AES measurement it can be considered as a particle. During the femtochemistry experiments, the fact that atoms are quantum objects can be ignored. As a corollary, the electron cannot be confined to a small region since its momentum would become very large. This is generally explained as the Heisenberg Uncertainty relation. The product of the uncertainties in the measurements of the position and momentum is comparable to the Planck's constant. The small experimental value of Planck's constant results in the predictions of the quantum action principle becoming identical with those of the classical action principle when large objects are considered. This is the reason large objects can be seen and experienced as either particles or waves. The quantum phenomena which seem to violate common sense cannot be experienced at large dimensions.

In considering an experiment, it was pointed out that it is quite often not possible to isolate the experiment from all external non-local influences. It thus becomes a reasonable requirement that the non-local causes be physical. This in turn means that the signals from outside the experimental setup take a finite time to reach the experimental setup. This logic when applied to the least action principle results in the special theory of relativity, which showed that the maximum velocity for the transfer of information (signal) is the velocity of light. Relativistic correction provides a conceptual basis for the experiment to be primarily influenced by the local conditions and for a finite velocity (velocity of light) for signals. One famous consequence of the relativistic principle is the mass energy equivalence ($E=mc^2$). It is well known that this equation explains the

large energy generated in an atomic bomb. Relativistic corrections are not very important for most large objects. The only objects which can have velocities comparable with the velocity of light are quantum objects like electrons and photons (light itself).

The next important feature of quantum mechanics can be understood only by appreciating the mass energy equivalence. Electrons as they move can emit and absorb photons. Photons can create electron-positron pairs. The positron is a particle with the same mass as the electron but with an opposite charge. The pair recombine to create a new photon. This ability of electrons and photons results in the everyday experience of attraction and repulsion of charges. Charge is the consequence of the ability of electron to create a photon. In technical language the electron couples to a photon. The relativistic principle can be explained on this basis. When a charge oscillates, another charge can respond to the movement. This is because photons can be exchanged between the two charges. These photons convey the information regarding the movement of the first charge to the second. This takes place at the velocity of light when these photons called the virtual photons travel over large distances from one charge to another.

Angular momentum and energy are both quantized and conserved. Thus the principles of conservation are valid for quantum objects also. \emptyset being a complex quantity introduces an extra continuous symmetry in the physical laws. $\emptyset\emptyset^*$ is the only physically relevant parameter. If \emptyset is multiplied by a factor $e^{i\epsilon}$, \emptyset^* is multiplied by $e^{-i\epsilon}$. $\emptyset\emptyset^*$ is not changed for any value of ϵ . As discussed earlier, this is a continuous symmetry. This symmetry in turn results in the conservation of charge. The principle of relativity has another very profound consequence. Pauli proved the spin statistics theorem which states that as a consequence of the theory of relativity, only two types of quantum objects can exist. Those which have an integral spin are called Bosons and those with half integral spin are called Fermions. Electron is a Fermion with a spin $\frac{1}{2}$ and photon is a Boson with a spin of 1. Spin normally corresponds to a rotation of the object around itself, much like the spinning of the earth. However, the quantum complexity continues. A particle with integral spin, a photon for

example with spin 1 behaves as if the object returns to the original state after a rotation of 2π . This appears to preserve common sense. However, the a particle with half integral spin, an electron with spin $\frac{1}{2}$ for example behaves as if it returns to the original state after a rotation of 4π . A rotation of 2π changes the sign of the wave function ψ . Such a mathematical entity is called a spinor. An electron behaves like a spin $\frac{1}{2}$ particle but this only refers to predicting the experiments successfully. The behavior cannot be described in a classical sense.

Pauli's theorem shows that Fermions have half integral spin and that Bosons have integral spin. This results in the ψ for a many particle system of being symmetric for bosons and anti-symmetric for Fermions. This mathematical statement has a very important physical consequence. As consequence of this symmetry, two Bosons can occupy the same location in space. Two Fermions cannot do so. The ability of many Bosons to occupy the same location of space results in lasers and superconductors. The inability of two electrons with the same energy and spin to occupy the same location of space is called the Pauli Exclusion Principle

Electrons exchange virtual photons with the nucleus of the atoms. Due to this, they are attracted towards the nucleus. Their energy is lower, the closer they are to the nucleus. However, as mentioned before, due to the uncertainty principle, the velocity of the electrons would be increased if they are confined to the space very close to the nucleus. Further, the exclusion principle would also cause the electrons to occupy different locations even if the energy would be slightly higher. The attraction is balanced by the repulsion due to these two causes.

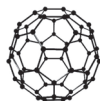
Thus, when a number of electrons are in the same region of space they are distributed in one or more quantum energy states. The arrangement of these energy states leads to the formation of all the elements in the periodic table. In an atom or a molecule, corresponding to each of these energy states, the electron has a probability for being present in a region of space around the positive charge of the nucleus. The region of space is called the orbital. Strictly speaking, an orbital is a mathematical quantity; the statistical probability of detecting the electron in a particular region of space.

However, the electron in the atom can be carefully monitored, without causing it to escape from the particular orbital. The electron can be repeatedly detected in the same orbital. Then the probability corresponds to the electron density. Experimentally observed electron densities can be confirmed to closely resemble the mathematically derived orbitals.

The orbitals are called atomic orbitals when electrons from an atom are considered. When the electrons in a molecule, which is a combination of atoms are considered, these are called molecular orbitals. Their nature and location define the properties of the bonding. This in turn defines the properties of the materials. It has been pointed out that when carbon atom exists individually, the energy states are different from those observed in the presence of four other carbon atoms. These are called sp^3 hybridized orbitals because they appear to be formed replacing the single s and three p orbitals of carbon atom. The bonds between carbon atoms represent overlapping regions of the sp^3 orbitals of the respective atoms. These bonds would be located at angles of 109° to one another. The consequences for the properties of diamond have been discussed earlier. When the electrons are localized preferentially on one atom rather than the other, the situation can be approximately described as transfer of an electron from one atom to another. This is called the formation of an ionic bond. Thus in the presence of a chlorine nucleus in the neighborhood, the 11th electron in a sodium atom will be found to occupy the space around the chlorine atom. We can more conveniently say that the electron is transferred from the sodium atom to the chlorine atom. The molecular orbital may be existing equally in the region of the two atoms. This is called a covalent bond. The two electrons in a hydrogen molecule occupy an orbital. The electron density is equal at both the hydrogen atoms. When a bond between hydrogen and oxygen is considered, the density is not exactly equal. There is partial transfer of electrons. These changes in the energy levels are observed in the XPS analysis which enables the identification of the bonding between atoms. When the electron density between two molecules of water is distorted, the influence is referred to as the formation of a hydrogen bond. The region of space occupied by an electron in one

water molecule is influenced by the presence of another water molecule in the neighborhood. The importance of hydrogen bonding for biological molecules has been discussed earlier.

Common sense requirements for an experimental approach have defined the present physical theories. Quantum mechanics is extremely competent in predicting the results of the experiments of physics. At the current level of understanding the accuracy is an astounding one part in several billions. This provides a theory which can calculate the distance between the equator and the pole to an accuracy of the thickness of human hair. At the same time many of the statements made violate common sense. It should be noted that these theories are not without an underlying common sense. The success in the development of new materials is a very practical proof of the use of these strange theories of physics.



Glossary of Some Technical Terms

In the text, most technical terms have been explained when they are introduced. However, some terms have been defined precisely below for additional clarity

Radio carbon dating	Method of determining the time elapsed since the death of a living organism by measuring the quantity of radio active isotope $^{14}\text{C}_7$ present.
Pastoral societies	Societies where humans live by keeping herds of goats, cows or other milk producing animals.
Darwinian adaptation	The particular attribute of a living organism which increases the number of offspring and hence improves the chances of survival of the species.
Draught animals	Animals like oxen and horses used for providing the power to move vehicles and ploughs.
Electrolytic refining	Method of producing a pure metal by passing electricity through a liquid containing a metal compound or electrolyte.
Quantum mechanics	The theory used to predict the results of experiments involving the smallest parts of matter (atoms and sub-atomic particles) and of light (photons).
Electrons	The smallest negatively charged constituent of matter outside the nucleus of an atom which controls the binding of atoms to form molecules.
Orbitals	The region in space where an electron can be confirmed to exist.

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Hybridization	Mixing of orbitals of electrons of approximately equal energy when they are located near each other is space
Transistor	A semiconducting device that permits amplification of a current and thus the most important component of modern electronic devices.
Line spectrum	The precisely defined colour or wavelength of light emitted or absorbed by atoms.
Ferromagnetism	The interaction between atoms (or electrons) responsible for exhibiting the magnetic property of orienting with the earth's magnetic field.
Superconductivity	The interaction between electrons that permits them to move in a solid without losing energy and thus exhibiting zero resistance.
Biopolymers	Long chains of nucleotides or amino-acids that are the primary building blocks of living organisms.
Bandgap	The range of energies which are not possessed by electrons in a solid.
Interference	The process whereby energy from one part of the wave is transferred to another part due to interaction with a second wave.
Diffraction	Transfer of a small amount of energy in the wave into a different direction due to an obstacle whose dimension is comparable to the wavelength.
Tunneling	The quantum mechanical process of movement through a region of higher potential energy (barrier) without actual increase of particle energy which could enable it to go over the barrier.
Tempering	Increasing the strength of steel or other metallic alloys by heating to high temperatures.
Mean free path	The average distance traveled by a particle between successive collisions.
Statistical mechanics	The theory of determining the properties such as temperature and pressure in terms of the energies of a large number of individual particles.

Glossary

Self organization	The exhibition of order of arrangement of small individual particles over large dimensions due to interactions between individual particles.
Genetic Engineering	Artificial transfer of genetic information from one organism to another of the same or different species.
Uncertainty principle	The manifestation of quantum nature whereby experimental determination of energy or momentum to a specific degree of accuracy limits the accuracy with which time or position can be determined.
Vacuum	Reducing the number of particles of atmosphere in a volume by a factor of 10^{10} (High Vacuum) or 10^{13} (Ultra High Vacuum) compared to the number at atmospheric pressure.
Transient states	Molecules which exist for a very short time during chemical reactions.
Diffraction limit	The limit on the minimum size of an object that can be observed due to diffraction of scattered waves.
Reciprocal space	A mathematical construction that helps in visualizing the Fourier (sinusoidal) components of electron density which correspond to the intensities of diffracted energy.
Fourier analysis	The method of decomposing a required signal into the sum of a sinusoidal components with multiples of a base frequency.
Electron density	The number of electrons existing in unit volume.
Phonons	The quantum mechanical object representing the smallest energy of a vibrating bond between atoms in a solid also called a lattice vibration.
Hydrogen bonding	A weak bond formed between electron densities of two molecules usually through a molecule of water.
Ionic bond	Bond formed between atoms where there is almost complete transfer of electronic charge from one atom to another.

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Covalent bond	Bond formed between atoms when the individual electrons of the two atoms are shared by the two atoms.
Van der Waal forces	Weak electrostatic forces between molecules which does not alter the electronic orbitals of the individual atoms or molecules.
Genetic code	The universally used coding between the sequence of three nucleotides in the DNA and the amino acid constituting the protein and determines the growth and functioning of the organism.
Codon	The three member sequence of nucleotides which represents the amino acid.
Anti-codon	The complementary sequence of three nucleotides in the codon.
Feedback process	The process occurring in living systems whereby an output corresponding to a sensory input is generated to alter the environment towards a preferred state.
Primary structure	The sequence of amino acids constituting the protein.
Secondary structure	The three dimensional shape into which the protein folds due to hydrogen bonding and Van der Waaal forces.
Chemical osmosis	The process conversion of the changes in concentration of ions across a membrane into useful energy.
Prokaryotes	The primitive living organisms where the DNA is not confined in the nucleus.
Eukaryotes	The living cells where the DNA is confined in the nucleus.
Probability	The numerical value of the chance of occurrence of a particular event when the experiment is repeated a large number of times.
Complex conjugate	A mathematical quantity obtained by changing the sign of the imaginary part of a complex number.

Suggestions for further reading

The book seeks to expose the young reader with the latest advances in science and explain the way these advances are used in developing new materials. A lot of the material referred to in the text is very new, since some of it is taken from research publications of the last few years. It is presumed not to be meaningful to give journal references in view of the targeted readership, except in a few cases when it became inevitable. It is suggested that in many cases, to locate further information, some of the terms can be used as keywords with a web browser like 'google' available on the internet. In any case, the World Wide Web is more easily accessible than published books which may not be available except in a really large library. However, some of the material available on the web may disappear without warning! I offer my apologies in case that happens.

Chapter 2 From nature to molecular design

A useful book which provides insight into new materials is "Made to Measure: New Materials for the 21st Century" by *Philip Ball*. The author has also written several other books "Designing the Molecular World", "Stories of the Invisible: A Guided Tour of Molecules" and "Life's Matrix: A Biography of Water" which could be good starting materials for learning about the materials revolution which is affecting our lives. A similar but slightly older book is "Tomorrow's materials" by *Ken Easterling*

Chapter 3 Nanomaterials and nanomachines

Highly readable accounts of nanomaterials can be found in "A look inside nanotechnology" prepared by the US department of Defense

and published as a special issue of AMPTIAC Quarterly Volume 6, Number 1 2002 http://amptiac.alionscience.com/pdf/AMPQ6_1.pdf and “Shaping the world atom by atom “ a document prepared by the inter-agency working group on nanoscience engineering and technology IWGN <http://www.wtec.org/loyola/nano/IWGN.Public.Brochure/> The famous lecture by Feynman given in 1959 is most useful and has been re-published a large number of times and is freely available on the internet for example at <http://www.zyvex.com/nanotech/feynman.html> “Nanotechnology: A Gentle Introduction to the Next Big Idea” by *Mark A. Ratner, Daniel Ratner, and Mark Ratner* is a good start for reading more about nanomaterials.

Chapter 4 Concepts of chemistry

The basic concepts of chemistry can be read in any text book on chemistry. I recommend the free electronic books available at http://en.wikibooks.org/wiki/Main_Page. The contribution of Einstein and the experimental work of Perrin are classic material that can be found in many textbooks on thermodynamics. A few web based sources which offer more easily readable versions are <http://www.bun.kyoto-u.ac.jp/~suchii/einsteinBM.html> and http://www.einsteinyear.org/facts/brownian_motion/fact_view which include some simulations. The femtochemistry work of *Dr Ahmed Zewail* is best appreciated in his own article “Femtochemistry : Past Present and Future” in *Pure and Applied Chemistry*, Volume 72, page 2219, (2000) or his Nobel lecture “Femtochemistry : Atomic scale dynamics of the chemical bond “ *Journal of Physical Chemistry* Volume 104A, page 5660 (2000). Similarly, the work concerning observation of the electronic orbitals can be found in the original publications, *Zuo, J. M., Kim, M., O’Keeffe, M. and Spence, J. C. H.* Journal “Nature” Volume 401, pages 49–52 (1999) and *M. Herz, F. J. Giessibl, and J. Mannhart* Physical Review B Volume 68, page 045301 (2003).

Chapter 5 Probing matter

One of the simpler books concerning materials characterization techniques is “Electron beam analysis of materials” by *M H Loretto*. The first few chapters provide a basic introduction to electron beam

interactions with a higher rigor. Many books are available for understanding the techniques discussed here. For example “A Guide to Materials Characterization and Chemical Analysis” by *J. P. Sibilio* offers a comprehensive discussion of the area of materials characterization for beginners.

Chapter 6 Physics of Living

The best introduction to fundamental biology is the book “A river out of Eden” by *Richard Dawkins*. It introduces Darwinian concepts in the most readable way. Kimball’s biology pages <http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/> and <http://w3.dwm.ks.edu.tw/bio/activelearner/index.html> are two web based sites for exhaustive and extremely readable information on biology. Wonderful animated descriptions of protein synthesis are available at <http://www.johnkyrk.com/DNAtranslation.html> and <http://gslc.genetics.utah.edu/units/basics/>. These are very useful in appreciating the intricacies of biology.

Chapter 7 Experimental method and principles of physics.

The best introduction to understanding quantum phenomenon for a student is “QED, The strange theory of light and matter”. *Richard Feynman*. Those curious about Neother’s theorem may look at the excellent site <http://www.emmynoether.com/>. The material is now presented in a new book “Symmetry and the Beautiful universe” by *L M Lederman and C T Hill*. The Hitachi site <http://www.hqrd.hitachi.co.jp/em/doubleslit.cfm> has a visual demonstration of the quantum mechanical uncertainty. A visit to this site would be most useful for all students and would be equivalent to several hours of reading text books on quantum mechanics.

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In the course of human history, man has continuously developed newer materials primarily to improve his tools. This quest originated with the use of naturally occurring stones and sticks which he shares with his cousin, the chimpanzee. Since then, the quest had resulted in the development of the miracles of ancient metallurgy and today has reached the nano dimension. Man currently has the ability to manufacture millions of electronic devices on a small chip of silicon, each of the transistor being as small as a few nanometers. He has also learnt to manipulate individual atoms and emulate the capabilities of living organisms which they acquired in the course of 3.5 billion years of organic evolution. These exciting capabilities in turn are the consequences of the fundamental understanding of physics, chemistry and biology. The book provides a bird's eye view of the saga of human materials development from the stone age to nanomaterials and genetic engineering and a coherent brief description of the science which underpins this development.



Dr S T Lakshmikumar obtained a Ph. D degree from Indian Institute of Science Bangalore joined the National Physical Laboratory, New Delhi as a scientist in the materials division. He has been a visiting scientist at the Ransellaer Polytechnic Institute, Troy, USA as a C V Raman Fellow in 1992. He began his research on metallic glasses and has continued research and development of

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